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POLYNUCLEAR AROMATIC COMPOUNDS FOR
HIGH TEMPERATURE LUBRICANTS

CHARLES F. RALEY, JR.

SOUTHWEST RESEARCH INSTITUTE

MAY 1956

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HIGH TEMPERATURE LUBRICANTS

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WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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ABSTRACT

The program of investigation of the class of aryl phosphate esters was continued. These materials possessed the most promising high-temperature properties of those examined. The aryl groups found to be the most thermally stable were phenyl, fluoro- and chlorophenyl, m-trifluoro-methylphenyl, 4-biphenylyl, dimethylphenyl, 5-indanyl and naphthyl. The simple phosphate structure was found to be quite stable. Pyrophosphates had the drawbacks of mediocre thermal and hydrolytic stability, although apparently possessing good oxidative stability.

Compositions prepared by reacting two or three different phenols with the proper amount of $POCl_3$ were also investigated. These compositions exhibited markedly lessened tendency to crystallization. Many of the compositions possessed properties almost identical to pure compounds having equivalent phenol proportions, and had the advantage of greater ease of preparation.

A total of nine fluids were prepared which possessed a liquid range of at least -20 to 800°F. Many of the compounds and compositions prepared, including others not meeting this liquid range, are considered to have potential use value.
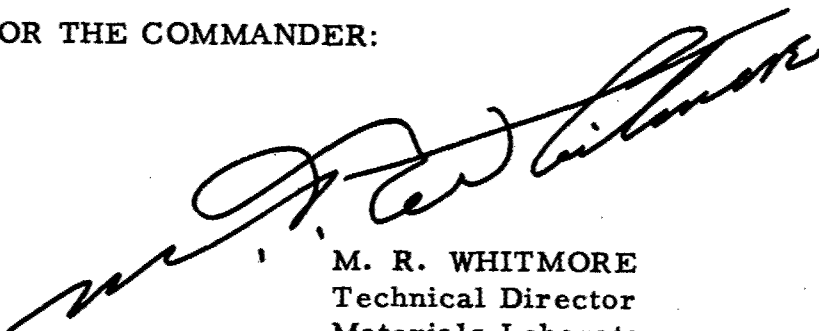
Several generalizations were drawn from the results of the over-all program. It was found that thermal and oxidative stability do not necessarily go together. Strongly polar substituents on the aromatic ring adversely affect hydrolytic stability. Two or more polar groups on a monocyclic ring adversely affect the thermal stability; one polar group on a bicyclic ring adversely affects thermal stability. A marked effect on such physical properties as boiling point, melting point, viscosity, etc., is observed, depending on the nature of the substituent groups. The more compact molecules generally have the greatest tendency to crystallize, with boiling point increasing with the molecular weight.

Indications were obtained of the possibility of inhibiting the oxidation of aryl phosphates by the addition of small amounts of heterocyclic phosphates.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

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I. INTRODUCTION

Since the speeds of aircraft and related equipment have been rapidly rising in recent years, the severity of the operating conditions, in particular higher temperatures, to which lubricants and hydraulic fluids are subjected has greatly increased. The fluids currently in use are becoming inadequate to meet these demands, particularly with respect to thermal and oxidative stability. Any increase in high-temperature properties should not excessively impair the low-temperature properties of a fluid, although reasonable concessions would be acceptable. The approach to the problem in this case has been the investigation of aromatic phosphate esters.

This project was started in August, 1952; the plan was to investigate the suitability of bi- and tricyclic liquid polynuclear aromatic compounds as high-temperature lubricants and related materials. A literature search was carried out, and from the 2400 compounds thus obtained, 14 were selected which seemed to be most promising. These compounds were representative of ethers, esters, ketones, alkylated aromatics, etc. Subsequently, three other compounds were added to the list. After screening these compounds for desirable properties, in particular thermal stability, the conclusion was reached that by far the most promise lay in the class of aryl phosphate esters.

The original phosphates were diphenyl naphthyl phosphates. The compounds possessed remarkable thermal stability, over 460°C (860°F), but happened to be low-melting solids. The work then followed the pattern of structural modification to achieve a liquid state at room temperature, defined as 35°C (95°F) or below, without sacrifice of the good thermal stability of the parent compounds. In the second year's work, during which time 42 phosphates were prepared, the requirement of fluidity at room temperature was easily met, and the goal was lowered to 0°F. This was also met.

During the third year's work a minimum liquid-range target of -20°F to 800°F was adopted. Other considerations, such as commercial feasibility and yield, although not direct requirements, began to appear more important. High thermal stability was no longer sufficient; oxidative stability and lubricity became important. Thus the work became increasingly oriented toward the production of a fluid of actual feasibility.

II. DISCUSSION

As in past reports, it seems most convenient to discuss the compounds

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prepared during the year in arbitrary classes, each having some significant feature in common. A listing of basic physical properties of all the compounds prepared is given in Table I. Those materials thought to possess properties of particular interest were subjected to further testing, the results of which are given in Table II.

The first such class, the pyrophosphates, consisted of the following compounds:

MLO 9567   Tetrakis(m-tolyl) pyrophosphate

MLO 9572   Tetraphenyl pyrophosphate

Both of these compounds were high-boiling liquids of much better than average fluidity, considering the molecular weights. The long flexible molecule may be the reason for this, and for the relatively good viscosity slopes. The tolyl compound, with a molecular weight of 538, had a pour point of -10°F and a slope of 0.778 from 100-210°F. The phenyl compound, molecular weight 482, had a pour point of -15°F and a 100-210°F slope of 0.744. No doubt the fluidity could be further improved by choice of different groups; however, it appears that the pyrophosphate structure itself has the drawback of possessing only fair thermal stability and poor hydrolytic stability. On the other hand, the oxidation stability of tetraphenyl pyrophosphate, as observed in a qualitative beaker test at 500°F, seems excellent. The phenyl compound underwent thermal decomposition at 362°C (684°F) and the tolyl compound at 333°C (631°F). The previously observed instability of the m-tolyl group (e.g., MLO 9518) results here in a lowering of the decomposition temperature of the whole molecule, as compared with tetraphenyl pyrophosphate. Perhaps, for a specific set of conditions, compounds of this type could prove useful.

The second class consists of chlorophenyl phosphates. Since it was known that tris(o-chlorophenyl) phosphate was a low-melting solid and tris (m-chlorophenyl) phosphate was a liquid,with both compounds possessing excellent thermal stability, it was thought desirable to attempt to prepare some analogous compound which would retain that thermal stability and possess fluidity equivalent to the meta compound with the low materials cost of the ortho compound. Therefore, all the possible simple chlorophenyl phosphates were prepared. These were:

MLO 9565   Bis(o-chlorophenyl) p-chlorophenyl phosphate

MLO 9566   Bis(p-chlorophenyl) o-chlorophenyl phosphate

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MLO 9580   Bis(p-chlorophenyl) m-chlorophenyl phosphate

MLO 9581   Bis(o-chlorophenyl) m-chlorophenyl phosphate

MLO 9584   Bis(m-chlorophenyl) p-chlorophenyl phosphate

MLO 9586   Bis(m-chlorophenyl) o-chlorophenyl phosphate

Tris(p-chlorophenyl) phosphate, a solid melting at 117°C (243°F), was not prepared. All of the above compounds possessed excellent thermal stability and, in general, their physical properties were fairly similar. All compounds containing two p-chlorophenyl groups were solid, while all those containing two m-chlorophenyl groups were liquid. Those containing two o-chlorophenyl groups showed the most deviation, with the third group exerting the controlling influence. One interesting fact was noticed: Compounds containing two or more m-chlorophenyl groups were infinitely soluble in poor solvents such as aliphatic naphtha and Dow Corning 550, a methyl phenyl silicone.

More specifically, bis(o-chlorophenyl) p-chlorophenyl phosphate, MLO 9565, was a solid melting at 43-45°C (109-113°F) and boiling at 457°C (854°F). The compound was thermally stable above its boiling point, 467°C (873°F) and was fairly viscous (49.6 cs at 100°F) although less so than tris (o-chlorophenyl) phosphate, which had a viscosity of 65.3 cs at the same temperature. Viscosity slope was mediocre.

The second compound in the list, MLO 9566, showing the effect of two p-chlorophenyl groups, melted at 48-50°C (118-122°F). It was thermally stable above 468°C (874°F), boiled at 475°C (854°F) and was somewhat less viscous than MLO 9565. Apparently o-chlorophenyl groups contribute to higher viscosity. The viscosity slope was also mediocre.

The next compound, MLO 9580, also contained two p-chlorophenyl groups, and despite the meta group was a solid, melting at 48-50°C (118-122°F). Thermal stability was again good, and the boiling point was high (455°C, 851°F), but the viscosity was significantly lower, 36.1 cs at 100°F. This was about 9 cs lower than the equivalent compound, MLO 9566.

The fourth compound, bis(o-chlorophenyl) m-chlorophenyl phosphate, MLO 9581, is somewhat interesting since it illustrates that, compared with tris(o-chlorophenyl) phosphate, the substitution of a meta for an ortho group dropped the pour point 10 degrees, to -5°F. Thermal stability and boiling point were high.

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The incorporation of two m-chlorophenyl groups, as in the next compound, MLO 9584, caused the pour point to drop to -20°F, the same as tris (m-chlorophenyl) phosphate. In this case, the tendency of the p-chlorophenyl group to cause crystallization was masked. Other properties are typical of the class. The liquid range is wider than the -20 to 800°F goal.

Finally, the o-chlorophenyl group in MLO 9586 was found to raise the viscosity slightly compared to MLO 9584, although the pour point was still -20°F. This compound also meets the liquid range goal. Tris(chlorophenyl) phosphates in general have high flash and fire points and autogenous ignition temperatures. The typical properties of the chlorophenyl derivatives are among the best.

The other pure compounds prepared constitute the third class. These were:

MLO 9573   Bis(o-chlorophenyl) m-trifluoromethylphenyl
               phosphate

MLO 9574   Diphenyl o-chlorophenyl phosphate

MLO 9575   Bis(p-chlorophenyl) m-trifluoromethylphenyl
               phosphate

MLO 9576   Bis(o-chlorophenyl) phenyl phosphate

MLO 9585   Bis(m-chlorophenyl) phenyl phosphate

MLO 9595   Bis(triphenylsilyl) benzene phosphonate

The first and third compounds listed, MLO 9573 and MLO 9575, are quite similar, differing only in the configuration of the chlorophenyl groups. In the first case, the compound was a fairly mobile liquid with a pour point of -30°F. The normal boiling point, however, was down to 378°C (712°F); the thermal stability was good, above 383°C (721°F). The volatility of this compound was considered excessive. In the case of MLO 9575, it was found that the volatilizing effect of the trifluoromethyl group was exhibited, but the two p-chlorophenyl groups resulted in a solid product, m.p. 51-53°C (124-127°F). The compound had exactly the same boiling point as the ortho analog, and was slightly more viscous. Thermal stability was excellent. The presence of m-trifluoromethylphenyl groups in a phosphate molecule greatly increases its

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solubility in such poor solvents as aliphatic naphtha and methyl phenyl silicone (DC 550).

The second and fourth compounds listed, MLO 9574 and MLO 9576, are also quite similar and illustrate the effect of substituting phenyl groups for o-chlorophenyl groups, taking tris(o-chlorophenyl) phosphate as the reference compound. When one chlorophenyl group was replaced by phenyl, the boiling point dropped to 435°C (815°F) and the pour point to -20°F. The viscosity was approximately halved. The flash point was lowered somewhat, to 520°F, but was still quite high, and the fire point remained above 760°F. This compound meets the -20° to 800°F liquid range target. When two phenyl groups and one o-chlorophenyl group were present, as in MLO 9574, the boiling point dropped again, to 424°C (795°F), as did the flash point, to 505°F. The pour point was lower, -30°F, as was the autogenous ignition temperature. One advantage of using phenyl groups is that the halogen content of the molecule is reduced, tending to reduce corrosion of such metals as copper under strong oxidizing conditions and at high temperatures. Although this compound barely misses the -20° to 800°F range, it could conceivably be useful in a closed system, where volatilization can be controlled.

With bis(m-chlorophenyl) phenyl phosphate, MLO 9585, a lower pour point, -25°F, was obtained than in the case of the corresponding o-chlorophenyl compound. The same held true for the boiling point, and the viscosity at 100°F was considerably lower. Following the pattern noted before, the bis(m-chlorophenyl) compound showed much greater solubility in poor solvents. Here also, the liquid range of -20° to 800°F was met.

The final compound, MLO 9595, is rather unusual. This is the only case where an attempt to prepare a Si-O-P bond was successful. The identification is mainly based on the molecular weight value. The compound was a high-melting solid, m.p. 190-191°C (374-376°F) which was very susceptible to hydrolysis and alcoholysis. The thermal decomposition temperature was 441°C (826°F).

In the fourth class are listed the binary chlorophenol phosphate compositions. This terminology refers to the fact that a mixture of two phenols are reacted with a stoichiometrical quantity of $POCl_3$ to form a composition containing four different molecular species, as follows:

$$3(ROH + R'OH) + POCl_3 \longrightarrow RRRPO_4 + RRR'PO_4 + RR'R'PO_4 + R'R'R'PO_4 + 3HCl$$
$$\text{(1 mole total)}$$

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The randomness of such a system tends to inhibit crystallization of any of the components. However, if a large enough proportion of a high-melting component is present, it is more likely to crystallize out. It is possible to overcome this by selecting the phenol ratio to minimize the formation of the high-melting component. This technique can be valuable in two cases: If a too-high melting point is the major unfavorable property of a compound, or if it is desired to avoid the two-step preparation of a mixed phosphate, since in many cases the properties of a mixed composition made with an equivalent phenol ratio correspond quite closely to those of the pure compound. These points will be illustrated in discussion of the following compositions, in which only isomeric chlorophenols were employed. The parenthetical notation after the name indicates the phenol ratio.

MLO 9568   Tris(chlorophenyl) phosphate, (1:1 ortho-para)

MLO 9569   Tris(chlorophenyl) phosphate, (2:1 ortho-para)

MLO 9570   Tris(chlorophenyl) phosphate, (4:1 ortho-para)

MLO 9571   Tris(chlorophenyl) phosphate, (5:1 ortho-para)

MLO 9582   Tris(chlorophenyl) phosphate, (1:1 ortho-meta)

MLO 9583   Tris(chlorophenyl) phosphate, (2:1 ortho-meta)

MLO 9587   Tris(chlorophenyl) phosphate, (1:2 ortho-meta)

The first four compositions comprise a series, prepared to study the effect of progressively increasing the ortho-para ratio, and to determine the lowest pour point attainable from o- and p-chlorophenyl phosphate mixtures. The economics of such compositions are very attractive. In the first case, MLO 9568, the reaction of 1.5 moles of o-chlorophenol, 1.5 moles of p-chlorophenol and 1.0 mole of $POCl_3$ led to the production of a mixture of 4 normally solid compounds:

$$1.5 \text{ } \underline{p}\text{-Cl}\emptyset\text{OH} + POCl_3 \xrightarrow[-3HCl]{} (\underline{p}\text{-Cl}\emptyset)_3PO_4 \qquad \text{m.p. } 117°C$$
$$+ \qquad\qquad\qquad\qquad\qquad\qquad\qquad (243°F)$$

$$1.5 \text{ } \underline{o}\text{-Cl}\emptyset\text{OH} \qquad\qquad (\underline{p}\text{-Cl}\emptyset)_2(\underline{o}\text{-Cl}\emptyset)PO_4 \qquad \text{m.p. } 48\text{-}50°C$$
$$(118\text{-}122°F)$$

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$$(\underline{o}\text{-}Cl\emptyset)_2(\underline{p}\text{-}Cl\emptyset)PO_4 \qquad \text{m.p. } 43\text{-}45°C$$
$$(109\text{-}113°F)$$
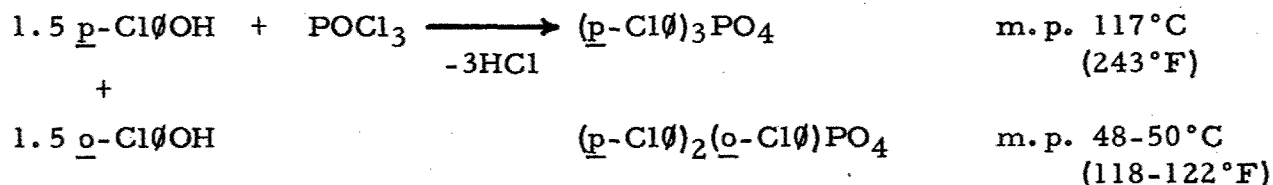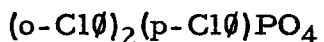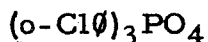
$$(\underline{o}\text{-}Cl\emptyset)_3PO_4 \qquad \text{m.p. } 34\text{-}35°C$$
$$(93\text{-}95°F)$$

In this case, a crystalline phase separated out, apparently tris(p-chloro-phenyl) phosphate. However, when the reaction was carried out using 2 moles of o-chlorophenol and 1 mole of p-chlorophenol, the product was an oil which in 1 year has exhibited no tendency to crystallize. This ratio tends to minimize the amount of tris(p-chlorophenyl) phosphate formed. All four of these ortho-para compositions resembled tris(o-chlorophenyl) phosphate in such properties as thermal stability, boiling point, density, viscosity, and flash point. The excellent thermal stabilities show that the heterogeneity of the system does not adversely affect the stability of the individual groups. Only the first one exhib-ited crystallizing tendencies and the three liquid compositions had slightly lower pour points than the pure tris(o-chlorophenyl) phosphate. The viscosity of the product increased with an increasing proportion of o-chlorophenyl groups, al-though the viscosity slopes decreased slightly. It seems rather certain that a pour point of 0°F will not be bettered significantly when only o- and p-chloro-phenyl phosphates are present. It should be mentioned therefore, that although it is possible to inhibit crystallization of a system, there is no apparent cor-relation between the melting point of a material and its viscosity-temperature characteristics, and it does not seem possible by this method to radically im-prove properties such as pour point, which are dependent on the viscosity-tem-perature relationship. However, in an application where better low-temperature fluidity is not required, these o-chlorophenyl:p-chlorophenyl compositions have many desirable properties.

The second series of three compositions, MLO 9582, MLO 9583 and MLO 9587, consisted of the o-chlorophenyl:m-chlorophenyl system. Here again, the three products were quite similar in boiling point, and had excel-lent thermal stability, although MLO 9587 boiled somewhat lower. The visco-sity dropped as the proportion of meta groups increased. An unexpected thing was that the 1:1 compound had a somewhat lower pour point than the 1:2 ortho-meta, although it may be mentioned that pour point determinations are not con-sidered to give results of high precision. Solubility in indifferent solvents in-creased with the proportion of meta groups. It is considered that MLO 9582 has a particularly favorable combination of properties, such as thermal sta-bility above 468°C (874°F), normal boiling point of 453°C (847°F), pour point, -20°F, low vapor pressure at 700°F (149 mm) and a flash point of 560°F. The

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liquid range surpasses the minimum goal. The present-day economics, however, are not particularly favorable, although they are certainly subject to change.

Class five is composed of compositions made from binary mixtures of phenols, where at least one of the phenols was other than a chlorophenol. A convention is used in nomenclature, wherein the name contains no number - indicating prefixes such as di- or bis-, but is followed in parentheses by the ratio of phenols, given in the same order as in the name. These were:

MLO 9577   o-Chlorophenyl m-trifluoromethylphenyl
            phosphate, (4:1)

MLO 9578   Phenyl o-chlorophenyl phosphate, (1:1)

MLO 9579   Phenyl o-chlorophenyl phosphate, (1:2)

MLO 9592   Phenyl o-chlorophenyl phosphate, (2:1)

MLO 9593   Phenyl m-trifluoromethylphenyl phosphate,
            (1:1)

MLO 9594   Phenyl m-trifluoromethylphenyl phosphate,
            (2:1)

The first composition, MLO 9577, represents an attempt to dilute the effect of the trifluoromethylphenyl group by making it a minor component. When the ratio is one trifluoromethylphenyl group to two o-chlorophenyl groups, as in MLO 9573, the compound is too volatile. It was thought that if a 1:4 phenol ratio were used, the composition might have a significantly lower pour point without excessive sacrifice of boiling point. A somewhat lower pour point was, in fact, observed, compared to tris(o-chlorophenyl) phosphate, which could be considered a reference compound (-5°F vs +5°F). The boiling point was moderately higher, 418°C (784°F) compared with the second reference compound, bis(o-chlorophenyl) m-trifluoromethylphenyl phosphate, MLO 9573, which boiled at 378°C (712°F). The boiling range was 30°C (54°F), which is not surprising considering the boiling points of the individual components of the mixture. From these observations, it appears that any decrease in pour point obtained by incorporation of the trifluoromethylphenyl group is coupled with a considerable increase in volatility. Compounds containing this group seem to have lower-than-average flash points. Other groups which lower the pour point, such as m-chlorophenyl or phenyl, do not seem to have this undesirable vola-

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tilizing effect to such a great extent.

The next three compositions constituted a series. The phenol ratio ranged from 2:1 phenol:o-chlorophenol to 1:2. The physical properties graded rather uniformly from one extreme of ratio to the other. Aside from boiling range, the similarity of physical properties between the pure compound and the composition having the same phenol ratio was surprising. The tabulation below illustrates this for a few key properties.

	NBP	Pour Point	Visc. @ 100°F	Flash Pt.
Diphenyl o-chlorophenyl phosphate	424°C (795°F)	-30°F	19.5 cs	505°F
Phenyl o-chlorophenyl phosphate, (2:1)	417°C (782°F)	-30°F	19.5 cs	510°F
Bis(o-chlorophenyl) phenyl phosphate	435°C (815°F)	-20°F	32.2 cs	520°F
Phenyl o-chlorophenyl phosphate, (1:2)	440°C (824°F)	-25°F	30.9 cs	530°F

One would expect the presence of triphenyl phosphate in the compositions to lower the flash points; this did not prove to be the case. In the case of MLO 9592, phenyl o-chlorophenyl phosphate, (2:1), the -20° to 800°F fluid range is barely not met, although the lower pour point could compensate for this in many applications. The yields were quite good, which could be an important consideration. The properties of MLO 9578, which has an equal ratio of phenyl and o-chlorophenyl groups, fell between the other two compositions. This material, as well as MLO 9579, met the -20 to 800°F liquid range requirement. All three are considered to have practical use possibilities.

The last two compositions listed, MLO 9593 and MLO 9594, were prepared to determine approximately the best fluidity possessed by an aryl phosphate. The phenyl and m-trifluoromethylphenyl groups had been shown to yield the most fluid compositions; therefore these two groups were combined in a composition. It may be remembered that the pure compound, triphenyl phosphate, was a solid, m.p. 49-50°C (120-122°F), and tris(m-trifluoromethylphenyl) phosphate was a thin oil, with a viscosity of 14.0 cs at 100°F, and a

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melting point of 13°C (55°F). The supercooled pour point was -35°F. When equal amounts of the two phenols were used in a composition, as in the case of MLO 9593, a very fluid oil was obtained with a pour point of -50°F and a viscosity of 11.3 cs at 100°F. This is the lowest pour point observed in this program. The normal boiling point was rather low, 369°C (696°F) but this might have been expected. The boiling range was rather narrow. The flash and fire points were down, to 450°F and 715°F respectively; this is one of the few phosphates prepared which will support combustion although the bulk temperature would have to be high. Viscosity slopes were about average.

The effect of reducing the proportion of m-trifluoromethylphenol was observed in the last composition, MLO 9594. The pour point was lowered to -45°F, although the 100°F viscosity rose only to 11.5 cs. The normal boiling point was up slightly, to 375°C (707°F). The flash point was considerably higher, at 485°F and the fire point was 735°F. This seems to be a better balance of properties than in the case of the preceding composition. These materials have possible utility as intermediate-range fluids.

The compounds in the final class were prepared by reacting ternary mixtures of selected phenols in a stoichiometric proportion with POCl$_3$. These were:

MLO 9588   Phenyl o-chlorophenyl m-chlorophenyl phosphate, (1:1:2)

MLO 9589   Phenyl o-chlorophenyl m-chlorophenyl phosphate, (1:3:2)

MLO 9590   Phenyl o-chlorophenyl 4-biphenylyl phosphate, (1:3:1)

MLO 9591   Tris(chlorophenyl) phosphate, (1:1:1 ortho-meta-para)

These ternary phenol compositions potentially contain ten different compounds, giving a system with enough randomness to inhibit crystallization of all but the most high-melting components. If the phenols differ much in molecular weight (excluding exceptions such as trifluoromethylphenol) there will be formed tris-phosphates of the low molecular-weight phenols as well as tris-phosphates of the high molecular-weight phenols, with a resultant large spread in the boiling range of the mixture, and possible crystal

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phase separation. The presence of low molecular-weight phosphates also contributes considerably to the total vapor pressure of the system, tending to reduce the normal boiling point.

The first composition, MLO 9587, had a low pour point, -25°F, but also a fairly low boiling point, 429°C (804°F). Absolute viscosity values were fairly low. The boiling range was rather wide. The phenol proportions in this case were chosen in an attempt to duplicate the properties of tris(m-chlorophenyl) phosphate, using equal quantities of phenyl and o-chlorophenyl groups to replace half the m-chlorophenyl groups. It was thought that the net effect of the lower-viscosity phenyl group combined with the effect of the high-boiling o-chlorophenyl group would be equivalent to a m-chlorophenyl group. This was roughly the case, as shown by the pour point, although the volatile constituents of the composition lowered the boiling point. The composition had the minimum -20 to 800°F liquid range but otherwise did not appear to be of particular interest.

In the case of MLO 9589, an attempt was made to use phenol proportions analogous to MLO 9582, tris(chlorophenyl) phosphate, (1:1 ortho-meta), but to improve the pour point without excessive sacrifice of boiling point. In the case of MLO 9582, the proportion was 1.5 moles of o-chlorophenol to 1.5 moles of m-chlorophenol. With MLO 9589, the proportion was 0.5 moles of phenol, 1.5 moles of o-chlorophenol and 1.0 mole of m-chlorophenol. The o-chlorophenol was made the major component in order to keep up the boiling point and minimize the quantity of m-chlorophenol used. No desirable changes were observed in properties, both the pour point and boiling point being less favorable.

The third composition, MLO 9590, was made primarily to find out if the 4-biphenylyl group could be used in small amounts to raise the boiling point of a mixture containing mostly o-chlorophenyl groups. An equal amount of phenyl groups was added to keep down the viscosity. Unfortunately it appears that some of the least desirable properties of the constituent compounds were displayed. The boiling point was fairly high, 458°C (856°F) but the pour point was +10°F and the boiling range was excessive. Higher boiling compounds were formed in the reaction but did not distill over. Since the highest molecular weight compounds were not present in the product, the molecular weight was lower than calculated. In effect, the properties of this composition were not as good as the simple tris(o-chlorophenyl) phosphate.

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The final ternary mixture, MLO 9590, had fairly good physical properties, which, however, were inferior in all but two respects to the similar binary composition, tris(chlorophenyl) phosphate, (2:1 ortho-meta). The absolute viscosities and solubilities were better for the ternary mixture; otherwise, the boiling point, pour point, volatility, and flash point were poorer. It is interesting that the mixture distilled like a pure compound, having a boiling range of only 2°C at 30 microns. This is, of course, due to the similarity of the phenols.

Since the only groups present in these compositions were those which had previously been shown to be thermally stable, it was expected that the compositions themselves would be thermally stable above their boiling points. This was, in fact, the case.

III. CONCLUSIONS

Of all the materials prepared, a total of 9 were found to possess the desired minimum liquid range of -20°F to 800°F. These materials were:

MLO No.	Name	Liquid Range
9553*	Tris(m-chlorophenyl) phosphate	-20° to 846°F
9576	Bis(o-chlorophenyl) phenyl phosphate	-20° to 815°F
9578	Phenyl o-chlorophenyl phosphate, (1:1)	-25° to 800°F
9579*	Phenyl o-chlorophenyl phosphate, (1:2)	-25° to 824°F
9582*	Tris(chlorophenyl) phosphate, (1:1 ortho-meta)	-20° to 847°F
9584	Bis(m-chlorophenyl) p-chlorophenyl phosphate	-20° to 837°F
9585	Bis(m-chlorophenyl) phenyl phosphate	-25° to 800°F
9586	Bis(m-chlorophenyl) o-chlorophenyl phosphate	-20° to 833°F
9588	Phenyl o-chlorophenyl m-chlorophenyl phosphate, (1:1:2)	-25° to 804°F

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In addition, diphenyl o-chlorophenyl phosphate, with a liquid range of -30° to 795°F, closely approached the goal.

The materials indicated by an asterisk were prepared in one gallon quantities for further evaluation by WADC, as were also MLO 9522, tris(o-chlorophenyl) phosphate and MLO 9574, diphenyl o-chlorophenyl phosphate. This does not indicate that the other compounds prepared were not interesting but that they did not possess the same balance of properties. Pour points as low as -50°F were observed, as in the case of MLO 9593, phenyl m-trifluoromethylphenyl phosphate, (1:1), and boiling points as high as 510°C (950°F), in the case of MLO 9563, bis(o-chlorophenyl) 4-biphenylyl phosphate. These extremes of liquid range, however, were obtained at the expense of the properties at the other end of the scale. For example, MLO 9593 had a boiling point of only 369°C (696°F) while MLO 9563 had a pour point of +45°F.

From the results obtained throughout the entire program, several generalizations may be drawn. The first generalization concerns thermal stability of phosphate esters. This property is particularly important in a high-temperature fluid since it is inherent in the structure of the molecule and cannot be improved by adding other materials. The basic phosphate structure, that is, the $\equiv PO_4$, is very thermally stable. Therefore, if the group attached to this structure is intrinsically unstable or if the bond between the group and the phosphate structure is unstable, the temperature at which decomposition occurs can be easily determined by vapor pressure deviation from the theoretical at that point. By ascertaining the stability of one or two groups, more or less by trial and error, a reference point is obtained. Phenyl groups are good for this purpose. Then a phosphate having two known stable groups plus an unknown third group may be prepared, and the decomposition temperature determined. Any instability shown may be ascribed to the third group. Another way is to prepare tris-phosphates, R_3PO_4, in which all groups are untested, and determine the point of decomposition. One difficulty in this case occurs when the tris-phosphate has properties which make it difficult to work with. For example, if the substituent group is large, the compound is likely to have an excessively high boiling point (causing decomposition on distillation), or high melting point, or very low solubility. Of all the groups examined, the following ones possessed the best thermal stability. A complete tabulation of all the groups examined and their approximate decomposition temperatures may be found in Part 2 of this report, published February, 1955.

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Phenyl	>485°C (905°F)	p-Chlorophenyl	>470°C (880°F)
m-Trifluoromethyl-phenyl	>430°C (805°F)	1,4-Phenylene	455°C (850°F)
3,4-Dimethylphenyl	>460°C (860°F)	5-Indanyl	>455°C (850°F)
3,5-Dimethylphenyl	>450°C (840°F)	1- and 2-Naphthyl	470-475°C (880-890°F)
o-Fluorophenyl	>430°C (805°F)	4-Biphenylyl	>510°C (950°F)
o-Chlorophenyl	>510°C (950°F)	Benzenephosphonate	>445°C (830°F)
m-Chlorophenyl	>465°C (870°F)		

It is interesting to note that the dimethylphenyl groups had very high decomposition temperatures while tolyl groups were observed to decompose at 370-395°C (698-743°F). Apparently if the substituent groups on the aromatic ring are non-polar, the stability of the whole structure is not lowered even when more than one group is present; in fact, the opposite seems true.

This is definitely not true when the substituent group is strongly polar. If a mononuclear aryl group carries two or more polar substituents, such as chlorine atoms, the thermal stability is markedly reduced. Thus the o-chlorophenyl group was stable above 510°C while the 2,4-dichlorophenyl group decomposed in the 430-440°C range. The pentachlorophenyl group was even poorer, decomposing at 372°C.

Phenylene derivatives appear to be only moderately stable. Here an aryl group carries two polar substituents. The para-phenylene derivatives are more stable than the meta. Somewhat surprisingly, the pyrophosphate structure shows only moderate stability.

In the case of a polynuclear aryl group, even a single polar substituent is deleterious, perhaps because the aromaticity of the system is weaker to begin with. As examples, the 1-naphthyl group decomposes at 470°C (880°F),

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the 2-chloro-1-naphthyl group at about 400°C (752°F), and the 2,4-dichloro-1-naphthyl group at 385°C (720°F).

The presence of a heterocyclic atom in an aromatic ring impairs thermal stability; for example, the 3-pyridyl group decomposes at about 360°C (685°F).

When oxidation stability is considered, many of the groups listed above no longer show up well. Alkyl substituents on aromatic rings would be expected to be unstable. The stable groups should be those which are unsubstituted, such as phenyl, or are substituted with an aromatic group, or halogen or perhalogenated alkyl group. One would expect, in the case of the halogen series, that iodophenyl groups would be least stable and fluorophenyl groups the most stable, in accordance with the ease of oxidation of the halogen atom itself. Although iodophenyl phosphates were not prepared, the bromophenyl phosphate was, and proved to be thermally unstable, the possibility being that bromine is easily detached as a free radical. If so, oxidation of such a system would be expected to occur rather readily.

Although oxidation information is rather fragmentary, the groups in the following list are either known to be stable or would be expected to be.

Phenyl	1- and 2-Naphthyl
m-Trifluoromethylphenyl	4-Biphenylyl
Fluorophenyl	Benzenephosphonate
Chlorophenyl	

Both the m-chlorophenyl and the naphthyl groups are probably less stable than the rest. Compounds containing these groups seem to darken on long standing at room temperature. Perhaps in the case of the naphthyl group, the lower aromaticity of one ring is responsible, causing the group to resemble an alkylated aromatic with respect to oxidative susceptibility. The case of the m-chlorophenyl group is perhaps more surprising. Probably the weak point is not the C-Cl bond but the C-O ester linkage. Here is an ortho-para directing group in a meta location. This results in a relatively high electron density in the ortho and para positions and a relatively low density in the meta position. If the primary mode of oxidation is free radical, it seems possible that a low electron density would result in little polarization of the C-O bond, which would

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make free radical formation more likely and thereby increase the ease of oxidation. In line with this, ortho-chloro and para-chlorophenyl groups would have high electron densities at the point of attachment, resulting in considerable polarization of the C-O bond, and would be less likely to form a free radical at that point and would be more resistant to oxidation. This, of course, is only speculation, but the experimental fact remains that the meta-chlorophenyl phosphate is more easily oxidized than the ortho or para-chlorophenyl compounds.

In view of the unremarkable thermal stability shown by tetraphenyl pyrophosphate, it is surprising that the compound appears to have excellent oxidation stability as observed in a qualitative beaker test at 500°F. Of course, this is below the thermal decomposition temperature of 362°C (684°F), but the appearance after prolonged heating was perhaps better than any other compound observed.

A factor which should be mentioned in any discussion of oxidation stability is that it is often possible to improve this characteristic by the addition of a suitable inhibitor. Many times a dramatic improvement is observed; aliphatic diesters by themselves would not be expected to be particularly stable to oxidation, yet the addition of phenothiazine in small amounts confers very satisfactory stability.

The inhibition of oxidation of aromatic phosphate esters has received very little investigation. From work done at the University of Virginia by Dr. J. W. Cole, on the oxidation of tris(o-chlorophenyl) phosphate, it appears that the usual inhibitors for diesters and mineral oils are not only not effective in phosphates but are pro-oxidant. However, on the basis of qualitative tests in this laboratory, carried out by heating an open beaker of fluid on a hot plate at 500°F, there is definite antioxidant activity shown by diphenyl 3-pyridyl phosphate, when added in small amounts to tris(o-chlorophenyl) phosphate and tris(m-chlorophenyl) phosphate. The improvement in the latter case was quite marked. It seems likely that the general class of heterocyclic aromatic phosphates would contain many compounds exhibiting antioxidant properties.

The correlation of structure with hydrolytic stability is difficult. It appears that the more electronegative the substituent on the ring, the poorer is the hydrolytic stability. Alkylated rings are more stable than halogenated rings. Meta halogenated rings are somewhat more stable than the corresponding ortho and para. Possibly this is affected by the reverse considerations which contribute to oxidative stability. It could be postulated that the

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greater the polarization of the C-O bond, the more susceptible it would be to ionic attack. Thus it would seem possible that the very factors which contribute to oxidative stability also contribute to hydrolytic instability. This is probably one of the inherent properties of an ester linkage. The bis-diaryl phosphates, $(RO)_2PO-O-X-O-PO(OR)_2$, appear to be relatively susceptible to hydrolysis. Here is an aromatic structure, X, bearing two substituents which, in view of the $\equiv P=O$ linkage, are probably electronegative. This accords with the previous speculation. Compounds containing the Si-O-P linkage seem to have exceedingly poor hydrolytic stability, if the identification of a compound prepared (MLO 9595) is correct.

Some generalizations may be made concerning the effect of structure on the physical properties of aromatic phosphate esters. Considering first the aromatic groups, it was found that the more symmetrical and compact the group, the more likely is the melting point of the compound to be higher. If the group is a chlorophenyl, for example, the meta group gives the lowest-melting phosphate, the ortho next, and the para highest. The closer the molecules can approach one another the more likely is crystalline orientation to occur. The three compounds listed below illustrate this:

Tris(p-chlorophenyl) phosphate	m.p. 117°C (243°F)
Tris(o-chlorophenyl) phosphate	m.p. 34-35°C (93-95°F)
Tris(m-chlorophenyl) phosphate	liquid, m.p. (?)

If the case of the homologous haloaromatic phosphates is considered, it appears that two factors are at work. The smaller the substituent, the greater would be the tendency to crystallize. However, there is also a tendency for the melting point to go up with increasing molecular weight, steric factors not being controlling. Thus, a minimum melting point would be expected in the middle of the series, as shown:

Tris(o-fluorophenyl) phosphate	m.p. 79-81°C (174-178°F)
Tris(o-chlorophenyl) phosphate	m.p. 34-35°C (93-95°F)
Tris(o-bromophenyl) phosphate	m.p. 83-84°C (181-183°F)

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Long molecules with numerous modes of rotation have lower melting points, presumably because of the steric repulsion factor. This is seen in such compounds as 1,3-phenylene bis(diphenyl phosphate) and tetraphenyl pyrophosphate. These are both liquids and possess relatively low pour points, 0°F and -15°F respectively, and better than average viscosity slopes.

Aryl phosphates bearing heterocyclic rings tend to be more fluid than those with carbocyclic rings. Alicyclic rings confer greater fluidity than aromatic rings.

The boiling points of aryl phosphates do not seem to be greatly affected by steric factors but correspond primarily to the molecular weight of the molecule. Thus in the series just listed, the calculated normal boiling points of the compounds were 417°C (783°F), 463°C (865°F), and 481°C (898°F) respectively. The respective molecular weights are 380, 430 and 563.

There was observed, however, a unique exception to this behavior. This was the m-trifluoromethylphenyl group. It appears that the CF_3 substituent caused a considerable reduction in intermolecular attraction, with marked reduction in boiling point, and viscosity, considering the relatively high molecular weight. The melting point reflects the higher molecular weight but is still low in comparison. When comparison is made with a sterically similar compound, the difference is notable.

	M. W.	N.B.P.	Viscosity @ 100°F	M.P.
Tris(m-chlorophenyl) phosphate	430	452°C (846°F)	27.6 cs	(?)
Tris(m-trifluoromethylphenyl) phosphate	530	366°C (671°F)	14.0 cs	13°C (55°F)

The presence of polynuclear groups or multinuclear groups considerably increases the melting and boiling points of a phosphate. This cannot be due primarily to molecular weight increase since, for example, the naphthyl group is not much heavier than chlorophenyl but produces a disproportionate increase in boiling point.

When the phosphonate configuration is compared to the phosphate, it is seen that a more compact molecule results, with less random motion. This tendency should increase as the configuration approaches that of the phosphine

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oxides. The end result is a higher melting point and boiling point, the latter indicating a greater intermolecular attraction. The following list illustrates this:

	M.P.	Pour Pt.	N.B.P.
Triphenyl phosphate	50°C (122°F)	-	385°C (725°F)
Diphenyl benzenephosphonate	76°C (169°F)	-	417°C (783°F)
Bis(o-chlorophenyl) phenyl phosphate	-	-20°F	435°C (815°F)
Bis(o-chlorophenyl) benzene- phosphonate	-	+10°F	444°C (831°F)

It deserves mention that the phosphate esters appear, in general, to be excellent lubricants, assuming results observed on specific examples are representative. A Ryder Gear Test carried out at Southwest Research Institute on a sample of tris(o-chlorophenyl) phosphate, MLO 9522, gave a rating of 3050 and 2760 lb/in. These two ratings were obtained from opposite faces of the gear teeth. These are considered to be excellent ratings, well above the 1700 lb/in specified in MIL-L-7808 B.

If these generalizations are valid, it should be possible in other cases to select a type of structure to meet different requirements, or at least to estimate the limitations imposed by the physical properties of aryl phosphate esters.

IV. EXPERIMENTAL

A. Apparatus and Methods

1. Thermal Stability. The method used for the determination of thermal stability involves the use of the isoteniscope to measure vapor pressure. In theory, the graph of log P (vapor pressure) versus the inverse of the absolute temperature is a straight line. When the compound starts to decompose, the vapor pressure increases non-uniformly, apparently due to the formation of volatile products, and departs from the straight line. This point of departure

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is taken as the thermal decomposition temperature. The isoteniscope is essentially a bulb attached to a U-tube manometer, and this to an air condenser. Both the method of determining thermal stability and the general design of the isoteniscope were obtained from WADC TR 53-45 "Synthetic Lubricants", University of Michigan, on WADC Contract No. W-33-038-ac-21457, dated December, 1952. By refluxing under vacuum the liquid being tested, the liquid accumulates in the U-tube, displacing the air present in the process. The isoteniscope is then cooled, and the liquid poured from the manometer back into the bulb, some liquid being allowed to remain to act as a liquid seal to exclude air. The process is repeated several times, to remove all traces of air. The temperature is then raised gradually, and the liquid legs in the manometer balanced by an applied external pressure. At a given temperature the applied pressure necessary to balance the manometer equals the vapor pressure. After considerable initial difficulty in eliminating sources of trouble in the apparatus, the method was found to be quite satisfactory, although tedious.

An air bath was tried at first for heating the isoteniscope, but was abandoned due to non-uniform temperature gradients. An aluminum block, heated by a flame, was found to give good results. The block is cylindrical and surrounded by a glass shield; the block is provided with suitable recesses for inserting the isoteniscope and observing the manometer and bulb.

2. Viscosity at 400°F and 700°F. In order to provide a 400°F bath for viscosity determinations, consideration must be given to the problems inherent in maintaining such a relatively high temperature. If a liquid medium heated by some external source is used, the main difficulty is selecting a medium of sufficiently satisfactory oxidative and thermal stability. Continued transparency of the bath liquid is also necessary. Rather than use this method with its attendant complications, it was decided to use a refluxing liquid in an insulated chamber to provide the constant temperature. A drawing of the apparatus is shown in Wright Air Development Center Technical Report 53-337, November, 1953, p. 23. The body of the apparatus is a double-walled chamber with provisions for evacuating the annulus, if desired. A side-opening accepts a condenser. The viscosimeter is inserted into the central and large side holes in the plug and secured by wooden clips. The plug is equipped with an inlet and outlet for passage of a cooling medium to condense any vapor leakage. An expansion bellows at the bottom of the jacket relieves strain at high temperatures. It was found, at the barometric pressure prevailing in San Antonio, that tetralin gave a vapor temperature of 400°F.

The 700°F determinations were carried out in the same apparatus, employing refluxing m-terphenyl to obtain the proper vapor temperature. This

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material was obtained from Monsanto Chemical Company, who formerly produced it under the trade name "Santowax M".

3. <u>Molecular Weight</u>. This property was determined by the cryoscopic method using benzene as a solvent.

4. <u>Flash and Fire Point</u>. The ASTM open cup procedure No. D 92-52 was used, except that a miniaturized cup was used instead of the standard cup. The wall thickness of the standard cup was retained, but the volume was reduced by reducing the inside diameter of the cup, keeping the height, upper flange diameter and base diameter constant. Therefore, the cross-section of the small cup resembled a spool, with one end of the central opening closed. A sample of only about 20 cc is required, and results were in good agreement with the standard cup.

5. <u>Solubilities</u>. The solvent was added dropwise to a sample of about 2 gm of the material being tested. If the sample blended with the solvent under the continuing dilution, the sample was rated "infinitely soluble". If the sample did not blend with the solvent, a second technique was used. This method was to add the sample dropwise to a known weight of solvent and observe the point where cloudiness occurs. The sample weight was obtained by difference.

If, as in the case of water, the solubility of the sample was less than 0.01 gm in 150 cc of solvent, the sample was termed "insoluble".

6. <u>Hydrolytic Stability</u>. The procedure given in MIL-L-6387A, Section 4.4.8, p. 7 was used. The conditions, however, were too stringent for the compounds and such extensive hydrolysis occurred that neutralization numbers of the water and oil phases could not be obtained.

7. <u>Autogenous Ignition Temperature</u>. A 125 ml Erlenmeyer flask was placed in a 4-inch porcelain evaporating dish containing about one-half its volume of molten lead. The dish was heated with a gas-oxygen torch. The temperature was gradually raised and at intervals a drop of sample was dropped into the flask. The temperature at which the liquid ignited was taken as the autogenous ignition temperature. The temperature was determined by bracketing with compounds of known AIT. Since most of the compounds prepared had an AIT over 1400°F, which was the maximum workable temperature of the apparatus due to softening of the Pyrex flask, most are merely reported as >1400°F. Those igniting below that temperature are bracketed in a range determined by two known compounds.

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8. <u>Vapor Pressure at 210°F, 400°F and 700°F</u>. These values were obtained by extrapolation of the vapor pressure curves obtained during the thermal stability tests.

9. <u>Pour Point</u>. This determination was carried out according to ASTM Test D 97-47.

B. <u>Chemical Syntheses</u>

1. <u>Bis(o-chlorophenyl) p-chlorophenyl phosphate.   MLO 9565.</u>

To a solution of 128.5 gm (1 mole) of p-chlorophenol in 200 cc of pyridine was added 337.5 gm (1 mole) of di-o-chlorophenyl phosphoryl chloride. The flask containing the acid chloride was rinsed twice with 100 cc portions of pyridine and these portions added to the reaction mixture. The reaction mixture became quite hot, and on cooling a voluminous crystalline precipitate of pyridine hydrochloride formed. After standing for 15 hours the slurry was vacuum-filtered and the precipitate washed with anhydrous ether. The ether solution was combined with the original filtrate. The filtrate was then refrigerated for 15 hours and the second crystal crop filtered off and washed as before. Further refrigeration produced no further crystallization.

The filtrate was then stripped of volatiles by distillation to a flask temperature of 180°C at atmospheric pressure followed by distillation to 210°C flask temperature under aspirator vacuum (ca. 30 mm). Two vacuum distillations gave 287.8 gm of product, a colorless, somewhat viscous oil, b.p. 202-203°C/0.035 mm, n_D^{27} 1.5808, d_4^{25} 1.4063. On standing, the product crystallized to a solid, m.p. 43-45°C. The molecular weight was 422 obsd. 429.5 calc. The yield was 67%.

2. <u>Bis(p-chlorophenyl) o-chlorophenyl phosphate.   MLO 9566.</u>

To a solution of 245.8 gm (0.728 moles) of di-p-chlorophenyl phosphoryl chloride in 200 cc of pyridine was added 93.5 gm (0.728 moles) of o-chlorophenol (redistilled, b.p. 168-170°C) dissolved in 200 cc of pyridine. The solution became quite hot. After the initial heat of reaction had subsided, the solution was brought almost to reflux, then allowed to stand for 15 hours. After the addition of one-fourth pound of anhydrous ether, the reaction mixture was filtered. (Pyridine hydrochloride is insoluble in anhydrous ether.) The filter cake was washed with one-half pound of anhydrous ether and the combined filtrates refrigerated for 15 hours. The second crystal crop was filtered off and the vola-

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tiles removed by distillation at atmospheric pressure to 225°C (flask temperature) followed by distillation to 210°C (flask temperature) at aspirator vacuum.

Two vacuum distillations gave 245.8 gm of product, a somewhat viscous, colorless oil, b.p. 205°C/0.05 mm, n_D^{27} 1.5803, d_4^{25} 1.4083. On standing, the product crystallized, m.p. 48-50°C. The molecular weight was 424 obsd; 429.5 calc. The yield was 78.5%.

3. Tetrakis(m-tolyl) pyrophosphate. MLO 9567.

A. Di-m-tolyl hydrogen phosphate. A mixture of 200 gm (0.675 moles) of di-m-tolyl phosphoryl chloride and 1.5 liters of 5% NaOH was heated to reflux until the oil layer dissolved. The solution was then acidified with 300 cc of 6N HCl, whereupon a white oil separated out. The solution was then extracted six times with 100 cc portions of CCl_4. The CCl_4 solution was then extracted four times with 200 cc portions of water and dried over anhydrous $MgSO_4$.

The solution was then filtered and the CCl_4 distilled off, leaving an orange oil. This oil was insoluble in petroleum ether, indicating the absence of m-cresol, and could not be induced to crystallize. It was used in this form. The yield was 164.2 gm or 87.5%.

B. Tetrakis(m-tolyl) pyrophosphate. To a solution of 164.2 gm (0.591 moles) of di-m-tolyl hydrogen phosphate in 200 cc of anhydrous benzene was added a solution of 175 gm (0.591 moles) of di-m-tolyl phosphoryl chloride in 50 cc of benzene, followed by the addition of 46.7 gm (0.591 moles) of pyridine in 50 cc of benzene. The temperature rose at once and pyridine hydrochloride precipitated. Then 200 cc of benzene was added and the solution allowed to stand for 15 hours. The pyridine hydrochloride was filtered off and washed with benzene. The filtrate was stripped of volatiles under aspirator vacuum to a flask temperature of 175°C.

Two vacuum distillations then gave 164.5 gm (51.7% yield) of product, a colorless, rather viscous oil, b.p. 252-265°C/0.03 mm, n_D^{27} 1.5517, d_4^{25} 1.2331. The molecular weight was 547 obsd; 538 calc.

4. Tris(chlorophenyl) phosphate, (1:1 ortho-para). MLO 9568.

To a mixture of 289 gm (2.25 moles) of p-chlorophenol, 289 gm (2.25 moles) of o-chlorophenol and 228.6 gm (1.49 moles) of $POCl_3$ in a one-liter

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flask equipped with a thermowell and 80 cm reflux condenser was added 8 gm of anhydrous $MgCl_2$ (ca. 1 wt% of total reactants). The reaction mixture was heated to 200°C in one hour, kept at that temperature for 7 1/2 hours, then allowed to cool.

The mixture was stripped up to 250°C (flask temperature) at 33 mm. Two subsequent vacuum distillations yielded the product, a colorless oil, b.p. 215-217°C/0.03 mm, $n_D^{26.5}$ 1.5806, d_4^{25} 1.4083. The molecular weight was 422 obsd; 429.5 calc. On standing, a solid phase crystallized out, forming a slurry. The yield was 515.7 gm, or 80% of theory.

5. Tris(chlorophenyl) phosphate, (2:1 ortho-para). MLO 9569.

A mixture of 385.5 gm (3 moles) of o-chlorophenol, 192.8 gm (1.5 moles) of p-chlorophenol, 228.6 gm (1.49 moles) of $POCl_3$ and 4 gm of powdered an-hydrous $MgCl_2$ was placed in a one-liter, 2-neck, round bottom flask equipped with an 80 cm reflux condenser and a thermowell. The temperature was brought to 200°C and held there for 17 hours. Aspirator vacuum was then applied to the top of the condenser for one hour to drive the reaction to completion, the flask temperature being held at 180-190°C. The mixture was then stripped by distillation under aspirator vacuum to a flask temperature of 265°C.

Two vacuum distillations then gave 551.6 gm of product, a colorless oil, b.p. 191-208°C/0.03 mm, $n_D^{26.5}$ 1.5811, d_4^{25} 1.4081. The molecular weight determination gave a value of 430 obsd; 429.5 calc. The yield was 85.6%.

6. Tris(chlorophenyl) phosphate, (4:1 ortho-para). MLO 9570.

A mixture of 462.6 gm (3.6 moles) of o-chlorophenol, 115.7 gm (0.9 moles) of p-chlorophenol, 228.6 gm (1.49 moles) of $POCl_3$ and 4 gm of pow-dered anhydrous $MgCl_2$ was placed in a one-liter, 2-neck, round bottom flask equipped with an 80 cm spiral condenser and thermowell, and heated to 200°C. The mixture was kept at that temperature for 3 hours, then reduced to 165°C, the heating being continued for 15 hours. The condenser was left in place and aspirator vacuum was applied to the outlet to strip out HCl and complete the reaction without losing reactants. The temperature at this time was about 180°C. The degassing was continued for 2 hours.

The mixture was allowed to cool somewhat, then stripped by distilla-tion to a flask temperature of 285°C under aspirator vacuum. It was then vacuum-distilled twice to give the final product. This was a colorless oil, b.p. 209-214°C/0.035 mm, $n_D^{26.5}$ 1.5816, d_4^{25} 1.4084. The molecular weight was 423 obsd; 429.5 calc. The yield was 553.5 gm, equivalent to 85.9%.

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7. Tris(chlorophenyl) phosphate, (5:1 ortho-para). MLO 9571.

In a one-liter, 2-neck, round-bottom flask equipped with an 80 cm reflux condenser and a thermowell was placed a mixture of 481.9 gm (3.75 moles) of o-chlorophenol, 96.4 gm (0.75 moles) of p-chlorophenol, 228.6 gm (1.49 moles) of $POCl_3$ and 4 gm of anhydrous $MgCl_2$. The mixture was heated to 200°C and held there for four hours. Aspirator vacuum was then applied to the top of the condenser and the mixture heated at 200°C for an additional ten hours. The mixture was then allowed to cool partially and stripped of volatiles by distillation under vacuum to a flask temperature of 295°C.

Two vacuum distillations then gave 545.2 gm (a yield of 84.7%) of product, a faintly yellow, somewhat viscous oil, b.p. 201-208°C/0.03 mm, $n_D^{26.5}$ 1.5816, d_4^{25} 1.4076. The molecular weight was 429 obsd; 429.5 calc.

8. Tetraphenyl pyrophosphate. MLO 9572.

A. Diphenyl hydrogen phosphate. A mixture of 268.5 gm (1 mole) of diphenyl phosphoryl chloride and 81.4 gm (ca. 2 moles) of NaOH in 1500 cc of water was refluxed with stirring until the acid chloride layer disappeared. The time required was one hour. The solution was filtered, then cooled. The filtrate was divided into two portions and each portion was acidified with 175 ml of 6N acid (HCl or H_2SO_4). An oil separated out and eventually crystallized on seeding. After a short period of refrigeration the crystals were filtered off and washed with cold water. The crystals were allowed to dry at room temperature. The m.p. was 51-52°C, which corresponded well with the literature value of 51°C (1). The yield was 258.4 gm, equivalent to 90.3% (of the dihydrate).

The product was then dehydrated. A distillation apparatus was set up, containing 286 gm (1 mole) of diphenyl hydrogen phosphate dihydrate in the distilling flask and ca. 150 cc of 85% H_3PO_4 in the receiver. The flask temperature was brought to 85-90°C with a vacuum of 0.03 mm being applied. The process was continued for 5 1/2 hours, the flask temperature rising to 110°C. The yield of crude diphenyl hydrogen phosphate was 234 gm, equivalent to 93.7%.

B. Tetraphenyl pyrophosphate. To a mixture of 234 gm (0.937 moles) of diphenyl hydrogen phosphate and 253 gm (0.943 moles) of diphenyl phosphoryl chloride, was added slowly with stirring a solution of 76.1 gm (0.963 moles) of pyridine in 200 cc of benzene. Complete addition required 15 minutes. Heat was liberated and crystals of pyridine hydrochloride formed. The mixture was stirred for 2.5 hours and allowed to stand for 15 hours.

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The crystals were filtered off. After stripping off volatiles by distillation, first at atmospheric pressure then under aspirator vacuum, to a head temperature of 98°C, the residue was vacuum-distilled. Two such distillations gave the product, a colorless oil, b.p. 223-235°C/0.02 mm, $n_D^{26.5}$ 1.5592, d_4^{25} 1.2963. The molecular weight was 485 obsd; 482 calc. The yield was 339.6 gm, equivalent to 88.5%.

9. Bis(o-chlorophenyl) m-trifluoromethylphenyl phosphate. MLO 9573.

To a solution of 122.1 gm (0.754 moles) of m-trifluoromethylphenol in one-half pound of pyridine was added 254.5 gm (0.754 moles) of di-o-chlorophenyl phosphoryl chloride. The flask containing the acid chloride was rinsed three times with a total of one-half pound of pyridine and the rinsing added to the reaction mixture. Considerable heat was liberated. After the initial reaction had abated, the mixture was heated almost to reflux for one-half hour. After cooling, the mixture was refrigerated for 20 hours.

A crystal crop had formed. One-half pound of anhydrous ether was added to the solution which was then refrigerated for an additional seven hours. It was then vacuum-filtered and the flask and crystals washed with one-half pound of anhydrous ether. The filtrate was again refrigerated for 20 hours.

The second crystal crop was filtered off and washed with a little ether. Further refrigeration did not produce more crystallization. The solution was stripped to 220°C (flask temperature) at atmospheric pressure, then to 210°C (flask temperature) at 37 mm.

Two vacuum distillations gave 100.1 gm of product, a pale yellow, fairly mobile oil, b.p. 157°C/0.04 mm, n_D^{25} 1.5185, d_4^{25} 1.4264. The molecular weight was 461 obsd; 463 calc. The yield was 28.7%.

10. Diphenyl o-chlorophenyl phosphate. MLO 9574.

To a solution of 269.3 gm (1.0 moles) of diphenyl phosphoryl chloride and 129.0 gm (1.0 moles) of o-chlorophenol in one pound of dry technical dioxane was added 118.5 gm (1.5 moles) of pyridine. The clear solution was heated to reflux, at which point turbidity appeared and phase separation occurred. On cooling and standing at room temperature the lower phase crystallized. The mixture was refrigerated for 15 hours then vacuum-filtered. The precipitate was washed with absolute ether and all filtrate fractions combined. These were again refrigerated for 15 hours.

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The small amount of precipitate which had formed was filtered off. The volatiles were distilled off the filtrate, first at atmospheric pressure, then to a head temperature of 160°C at aspirator vacuum. The residue was then vacuum-distilled twice to yield 279.8 gm of product, an almost colorless oil, b.p. 167-168°C/0.045 mm, $n_D^{23.5}$ 1.5716, d_4^{25} 1.2892, molecular weight 357 obsd; 360.5 calc. The yield was 77.5%.

11. Bis(p-chlorophenyl) m-trifluoromethylphenyl phosphate. MLO 9575.

·   To a solution of 162 gm (1.0 moles) of m-trifluoromethylphenol in one-half pound of pyridine was added 337.7 gm (1.0 moles) of di-p-chlorophenyl phosphoryl chloride dissolved in one-half pound of pyridine. Heat was evolved and crystals formed. The mixture was heated to reflux, allowed to cool, then refrigerated for 15 hours.

The crystal crop was filtered off and washed with absolute ether. The ether solution was added to the filtrate and the mixture refrigerated for 40 hours. After filtering off the second crystal crop, the solution was concentrated by distillation at atmospheric pressure, followed by stripping to a flask temperature of 150°C under aspirator vacuum (29 mm).

Two vacuum-distillations gave 275.5 gm of product, a colorless oil boiling at 171-179°C/0.025 mm, d_4^{25} 1.4171 (supercooled). On standing a short time, the oil crystallized to a white solid, m.p. 51-53°C. The molecular weight was 460 obsd; 463 calc.

12. Bis(o-chlorophenyl) phenyl phosphate. MLO 9576.

A mixture was made of 338.1 gm (1.0 moles) of di-o-chlorophenyl phosphoryl chloride, 94.4 gm (1.0 moles) of phenol and one pound of pyridine. After the initial heat of reaction had subsided, the mixture was heated almost to reflux, then allowed to cool.

After refrigeration for 15 hours the solution was filtered and the crystals washed with one-half pound of anhydrous ether. The ether washings were combined with the filtrate and the solution refrigerated again for 15 hours.

The second crystal crop was filtered off and washed with one pound of anhydrous ether. After combining the ether solution with the filtrate, the solution was refrigerated for 65 hours.

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The few crystals which had formed were filtered off and the volatiles stripped off by distillation, first to 150°C flask temperature at atmospheric pressure, then 265°C under aspirator vacuum. The residue was vacuum-distilled.

The product obtained after two distillations was a colorless oil, b. p. 178-179°C/0.035 mm, n_D^{26} 1.5767, d_4^{25} 1.3468, molecular weight 391 obsd; 395 calc. The yield was 245.8 gm equivalent to 62.2%.

13. o-Chlorophenyl m-trifluoromethylphenyl phosphate, (4:1). MLO 9577.·

In a one-liter, 2-neck, round-bottom flask equipped with an 80 cm spiral water-cooled reflux condenser and thermowell were placed 312.5 gm (2.432 moles) of o-chlorophenol, 98.5 gm (0.608 moles) of m-trifluoromethylphenol, 155.4 gm (1.013 moles) of $POCl_3$ and 2.8 gm of anhydrous $MgCl_2$ (about 0.5 wt%). The mixture was heated to 200°C, requiring one hour, and held there for 7 hours. It was allowed to cool.

Aspirator vacuum was applied to the top of the condenser and the flask temperature brought to 170°C, at which temperature reflux was constant. The heating was continued for 3 hours and then the mixture was allowed to cool. It was then stripped by distillation to a flask temperature of 265°C under aspirator vacuum. The residue was then vacuum-distilled twice.

The product was a colorless, refractive oil, boiling from 172-203°C/ 0.05 mm, n_D^{26} 1.5540, d_4^{25} 1.4156. The molecular weight was 455 obsd; 450 calc. The yield was 377.6 gm or 83% of theory.

14. Phenyl o-chlorophenyl phosphate, (1:1). MLO 9578.

In a one-liter, 2-neck, round-bottom flask equipped with a thermowell and 80 cm spiral reflux condenser was placed 141 gm (1.5 moles) of phenol, 192.8 gm (1.5 moles) of o-chlorophenol, 153.4 gm (1.0 mole) of $POCl_3$ and 2 gm (ca. 0.5 wt%) of anhydrous $MgCl_2$. The reaction mixture was brought to 200°C, heated for 7 hours and allowed to cool.

Aspirator vacuum was applied to the top of the condenser and the mixture heated to 170°C and kept at that temperature for five hours. It was then stripped by distillation to 250°C (flask temperature) under aspirator vacuum.

After two distillations the final product was a water-white refractive

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oil, boiling from 171-186°C/0.05 mm, n_D^{26} 1.5731, d_4^{25} 1.3132. The molecular weight was 365 obsd; 378 calc. The yield was 317.9 gm equivalent to 84.2% of the theoretical.

15. Phenyl o-chlorophenyl phosphate, (1:2). MLO 9579.

In a one-liter, 2-neck, round-bottom flask equipped with a thermowell and 80 cm spiral reflux condenser was placed 94 gm (1.0 mole) of phenol, 257 gm (2.0 moles) of o-chlorophenol, 153.4 gm (1.0 mole) of $POCl_3$ and 2.5 gm (ca. 0.5 wt%) of anhydrous $MgCl_2$. The mixture was heated to 200°C, requiring 1 1/4 hours, then maintained there for 4 1/2 hours. It was then allowed to cool.

The reaction was completed by applying aspirator vacuum to the top of the condenser and heating the mixture at 170°C for 4 hours. After cooling, the mixture was stripped of volatiles by distillation to 250°C (flask temperature) under aspirator vacuum.

The product was obtained after two vacuum distillations. This was a colorless oil, b.p. 180-195°C/0.05 mm, n_D^{30} 1.5747, d_4^{25} 1.3431. The molecular weight was 392 obsd; 395 calc. The yield was 319.9 gm or 81%.

16. Bis(p-chlorophenyl) m-chlorophenyl phosphate. MLO 9580.

A mixture was made of 263.1 gm (0.779 moles) of di-p-chlorophenyl phosphoryl chloride, 100 gm (0.779 moles) of m-chlorophenol and one pound of pyridine. The solution was heated to reflux, cooled, then refrigerated. After several days the pyridine hydrochloride was filtered off and washed with one pound of anhydrous ether. The filtrate and washings were combined and refrigerated for 15 hours.

The second crop of pyridine hydrochloride was filtered off. The filtrate was concentrated by distillation at atmospheric pressure then under aspirator vacuum. The residue was then vacuum-distilled.

The product, obtained after two distillations, was a colorless oil, b.p. 188-194°C/0.03 mm, $n_D^{25.5}$ 1.5795, d_4^{25} 1.3993. On standing, the product crystallized, becoming a white solid, m.p. 48-50°C. The molecular weight was 429 obsd; 429.5 calc. The yield was 273.3 gm, 81.5% of the theoretical.

17. Bis(o-chlorophenyl) m-chlorophenyl phosphate. MLO 9581.

A solution of 337.5 gm (1.0 mole) of di-o-chlorophenyl phosphoryl

chloride and 128.5 gm (1.0 mole) of m-chlorophenol in one pound of pyridine was heated to reflux, cooled to room temperature, then refrigerated for two days. Then the pyridine hydrochloride was filtered off the cold solution and washed with one pound of anhydrous ether. The combined filtrates were re-frigerated again for several days, filtered, and concentrated by distillation at atmospheric pressure and aspirator vacuum.

Two vacuum-distillations gave 371.7 gm of product, a colorless oil, b.p. 195°C/0.02 mm, n_D^{24} 1.5819, d_4^{25} 1.4029. The molecular weight was 431 obsd; 429.5 calc. The yield was 87.1%.

18. Tris(chlorophenyl) phosphate, (1:1 ortho-meta). MLO 9582.

In a one-liter, 2-neck, round-bottom flask fitted with a thermowell and 80 cm spiral reflux condenser was placed 192.8 gm (1.5 moles) of o-chlorophenol, 192.8 gm (1.5 moles) of m-chlorophenol, 153.4 gm (1.0 moles) of $POCl_3$ and 2.7 gm of anhydrous $MgCl_2$. The $MgCl_2$ was prepared by heat-ing $MgCl_2 \cdot 6H_2O$ for 30 minutes at 300°C. The reaction mixture was heated to 200°C in about one hour. Heating was continued at this temperature for 4 hours; then the reaction mixture was allowed to cool.

Then aspirator vacuum was applied to the top of the condenser, the mixture reheated to 200°C, and held there for 5 hours to complete the reac-tion.

The volatiles were removed by distillation to a flask temperature of 260°C under aspirator vacuum. The residue was vacuum-distilled twice to obtain the product.

The product was a very faintly yellow refractive oil, b.p. 192-201°C/ 0.06 mm, $n_D^{24.5}$ 1.5808, d_4^{25} 1.4005. The yield was 371.7 gm which is 86.5% of the theoretical. The molecular weight was 430 obsd; 429.5 calc.

19. Tris(chlorophenyl) phosphate, (2:1 ortho-meta). MLO 9583.

A mixture of 128.5 gm (1.0 mole) of m-chlorophenol, 257.0 gm (2.0 moles) of o-chlorophenol, 153.4 gm (1.0 mole) of $POCl_3$ and 2.7 gm of anhy-drous $MgCl_2$ was placed in a one-liter, 2-neck, round-bottom flask and heated to 200°C. The heating was continued for 5 hours. Then the mixture was stripped by distillation under aspirator vacuum to 260°C flask temperature. The product was obtained by two vacuum-distillations of the residue.

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The product was a colorless, refractive oil, b.p. 193-196°C/0.06 mm, n_D^{23} 1.5822, d_4^{25} 1.4050. The molecular weight was 430 obsd; 429.5 calc. The yield was 374.7 gm or 87.3%.

20. Bis(m-chlorophenyl) p-chlorophenyl phosphate. MLO 9584.

To a solution of 257 gm (2 moles) of m-chlorophenol in 500 ml of pyridine was added portionwise 245.5 gm (1 mole) of p-chlorophenyl phosphoryl dichloride. Considerable heat was evolved. The solution was heated to reflux, then allowed to cool.

After refrigeration of the solution, the pyridine hydrochloride crystals were filtered off and washed with anhydrous ether. The combined filtrate and washings were again refrigerated, yielding a small second crop of crystals. After removal of the volatile material by distillation under atmospheric pressure, and then under water aspirator vacuum, the residue was vacuum-distilled.

The product consisted of 349.6 gm of a water-white, refractive oil, b.p. 197°C/0.05 mm, n_D^{23} 1.5799, d_4^{25} 1.3974. The molecular weight was 433 obsd; 429.5 calc. The yield was 81.4%.

21. Bis(m-chlorophenyl) phenyl phosphate. MLO 9585.

To a solution of 257 gm (2 moles) of m-chlorophenol in one-half pound of pyridine was added 211 gm (1 mole) of phenyl phosphoryl dichloride. Another one-half pound of pyridine was used to rinse the acid chloride flask into the reaction flask. Considerable heat was evolved and two phases formed. The mixture was heated to incipient reflux, allowed to cool, and refrigerated.

The reaction mixture was filtered while cold and the crystal crop washed with anhydrous ether. The ether washings and filtrate were combined and again refrigerated. The second crystal crop was filtered off and washed with a little anhydrous ether. The filtrate and washings were combined and concentrated by distillation, finally under reduced pressure, then vacuum-distilled.

The product was turbid, and orange deposits were formed in the still head. (This was thought to be due to impurities such as phosphorus or arsenic compounds derived from the iron catalyst used to make the phosphoryl chloride.) The product was dissolved in one liter of benzene and washed three times with 200 ml portions of 5% HCl, then three times with 200 ml portions of water, and dried over anhydrous $MgSO_4$. The benzene was stripped off by distillation, finally to a flask temperature of 255°C under aspirator vacuum.

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Vacuum-distillation of the residue gave 278.2 gm of a cloudy colorless oil, b.p. 175-176°C/0.08 mm. The oil was clarified by slurrying with Celite and a little anhydrous $MgSO_4$, heating to 100°C for 30 minutes and vacuum-filtering through double paper. The filtrate was a clear, water-white, refractive oil, n_D^{23} 1.5741, d_4^{25} 1.3413. The molecular weight was 396 obsd; 395 calc. The yield was 70.5%.

22. Bis(m-chlorophenyl) o-chlorophenyl phosphate. MLO 9586.

To a solution of 264.9 gm (2.06 moles) of m-chlorophenol in 500 ml of pyridine was added 253 gm (1.03 moles) of o-chlorophenyl phosphoryl chloride. Heat was evolved and two phases separated out. After it had cooled to room temperature, the mixture was refrigerated. Then the pyridine hydrochloride was filtered off and washed with anhydrous ether. The filtrate and washings were combined and again refrigerated. After filtration and ether-washing of the second crystal crop, the washings and filtrate were stripped of volatiles to a flask temperature of 258°C under aspirator vacuum. The residue was vacuum-distilled twice.

The product was a colorless, cloudy oil, b.p. 195°C/0.10 mm. The oil was clarified by slurrying with filter-aid and filtering through double thickness paper. The oil, n_D^{26} 1.5790, d_4^{25} 1.4065, weighed 305.4 gm, equivalent to a yield of 69.0%. The molecular weight was 434 obsd; 429.5 calc.

Note: During the vacuum-distillations a brownish-orange deposit insoluble in water or acetone formed in the distilling head. A gaseous by-product was also observed which flashed spontaneously in air, had a metallic odor and was very toxic. The product had a peculiar metallic or garlic-type odor, probably due to the presence of the gas in solution. It is thought that this gas was phosphine or arsine, or perhaps both, or organic derivatives thereof. The source was probably arsenic or phosphorus impurities in the cold-rolled steel filings used as the catalyst in preparing o-chlorophenyl phosphoryl dichloride.

23. Tris(chlorophenyl) phosphate, (1:2 ortho-meta). MLO 9587.

In a one-liter, 2-neck, round-bottom flask equipped with a thermowell

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and 80 cm spiral reflux condenser was placed 257.0 gm (2.0 moles) of m-chlorophenol, 128.5 gm (1.0 mole) of o-chlorophenol, 153.4 gm (1.0 mole) of $POCl_3$ and 2.7 gm (ca. 0.5 wt%) of anhydrous $MgCl_2$ (prepared by heating 5.5 gm $MgCl_2 \cdot 6H_2O$ at 300°C for 30 minutes). The temperature was brought to 200°C and held there for 4 1/2 hours, then allowed to cool. Aspirator vacuum was applied to the top of the condenser and the mixture reheated; the equilibrium temperature was 180°C. After being heated for six hours the mixture was allowed to cool.

The mixture was stripped by distillation under aspirator vacuum to a flask temperature of 285°C. The weight of the distillate, probably phenolic, was 41.8 gm, equivalent to 0.326 moles of chlorophenol, or 0.108 moles of product, a loss of 10.8% yield. The loss is due to entrainment of $POCl_3$ in the HCl stream passing through the condenser.

Subsequent vacuum-distillation gave 320.7 gm of product, a faintly brownish-yellow oil, b.p. 193°C/0.05 mm, n_D^{26} 1.5797, d_4^{25} 1.4067. The molecular weight was 433 obsd; 429.5 calc. The yield was 74.7%.

24. Phenyl o-chlorophenyl m-chlorophenyl phosphate, (1:1:2). MLO 9588.

In a one-liter, 2-neck, round-bottom flask fitted with a thermowell and 80 cm spiral reflux condenser was placed 70.5 gm (0.75 moles) of phenol, 96.4 gm (0.75 moles) of o-chlorophenol, 192.8 gm (1.5 moles) of m-chlorophenol, 153.4 gm (1.0 mole) of $POCl_3$ and 2.6 gm (ca. 0.5 wt%) anhydrous $MgCl_2$. The mixture was heated to 200°C, requiring 1.5-2 hours and held there for 5 1/2 hours before allowing to cool. Then the mixture was refluxed under aspirator vacuum at 190°C for 4 hours followed by stripping to a flask temperature of 250°C under aspirator vacuum. The weight of stripped distillate indicated that a 9% loss of $POCl_3$ had occurred.

Vacuum-distillation then gave 305.0 gm of product, a colorless refractive oil, b.p. 183-207°C/0.05 mm; the main distillation plateau was 184-191°C/0.05 mm. The yield of product, n_D^{26} 1.5755, d_4^{25} 1.3622, was 75.5%. The molecular weight was 401 obsd; 404 calc.

25. Phenyl o-chlorophenyl m-chlorophenyl phosphate, (1:3:2). MLO 9589.

In a one-liter, 2-neck, round-bottom flask equipped with an 80 cm water-cooled reflux condenser was placed 47.0 gm (0.5 moles) of phenol, 128.5 gm (1.0 moles) of m-chlorophenol, 192.8 gm (1.5 moles) of o-chlorophenol, 168.7

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gm (1.1 moles) of $POCl_3$ and 2.7 gm of anhydrous $MgCl_2$. The mixture was heated to 210°C, requiring one hour, and held there for 3 hours. It was then cooled to 150°C and aspirator vacuum applied to the top of the condenser. The mixture was heated at 200°C for 2 hours; then it was stripped by distillation under aspirator vacuum to a flask temperature of 283°C.

It was then vacuum-distilled. The product was a pale yellow, refractive oil, b.p. 186-199°C/0.04 mm, n_D^{25} 1.5790, d_4^{25} 1.3833. The molecular weight was 413 obsd; 412 calc. The yield was 365.8 gm or 88.7% of the theoretical.

26. Phenyl o-chlorophenyl 4-biphenylyl phosphate, (1:3:1). MLO 9590.

In a one-liter, 2-neck, round-bottom flask equipped with an 80 cm spiral water-cooled reflux condenser and thermowell was placed 56.4 gm (0.6 mole) of phenol, 231.3 gm (1.8 moles) of o-chlorophenol, 102.0 gm (0.6 mole) of 4-phenylphenol, 168.7 gm (1.1 moles) of $POCl_3$ and 2.8 gm of anhydrous $MgCl_2$. The mixture was heated to 200°C in 1.5 hours and held there for 2 hours. Then after cooling to 150°C, aspirator vacuum was applied to the top of the condenser and the mixture reheated to 200°C and held there for 1.5 hours to complete the reaction.

After stripping off volatiles by distillation under aspirator vacuum, to a flask temperature of 264°C, the residue was vacuum-distilled.

The product was a viscous, colorless oil, b.p. 192-274°C/0.04 mm, n_D^{25} 1.5938, d_4^{25} 1.3493. A considerable residue remained in the flask which had not distilled by the time the flask temperature reached 304°C. The latter part of the distillate was very viscous. The molecular weight was 426 obsd; 434 calc. The yield was 313.8 gm or 72.3%.

27. Tris(chlorophenyl) phosphate, (1:1:1 ortho-meta-para). MLO 9591.

In a one-liter, 2-neck, round-bottom flask equipped with a thermowell and 80 cm water-cooled spiral reflux condenser was placed 128.5 gm (1 mole) of o-chlorophenol, 128.5 gm (1 mole) of m-chlorophenol, 128.5 gm (1 mole) of p-chlorophenol, 161.1 gm (1.05 moles) of $POCl_3$ and 1.4 gm of powdered anhydrous $MgCl_2$ (about 0.25 wt% based on total reactants). The mixture was heated, reaching 200°C in about one hour. After being maintained at this temperature for one hour, the mixture was allowed to cool to 60°C and aspirator vacuum was applied to the top of the condenser. The flask was then reheated to 200°C, held at that temperature for 3 hours and allowed to cool.

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Upon stripping to 260°C flask temperature, under aspirator vacuum, a distillate (phenols) weighing 28.8 gm was obtained, equivalent to 0.075 moles of product. This distillate was returned to the flask, together with 11.5 gm (0.075 moles) of $POCl_3$, and the reaction process repeated. On the second stripping, very little distillate was obtained.

Upon vacuum-distillation, 400.7 gm of product was obtained, a colorless, refractive oil, b.p. 204-206°C/0.03 mm, n_D^{20} 1.5828, d_4^{25} 1.4057. The molecular weight was 434 obsd; 429.5 calc. The yield was 93.4%.

28. Phenyl o-chlorophenyl phosphate, (2:1). MLO 9592.

In a one-liter, 2-neck, round-bottom flask equipped with a thermowell and an 80 cm spiral water-cooled condenser was placed 188 gm (2 moles) of phenol, 128.5 gm (1 mole) of o-chlorophenol, 168.8 gm (1.1 moles) of $POCl_3$ and 1.2 gm of powdered anhydrous $MgCl_2$ (about 0.25 wt% of total reactants). The mixture was brought to 200°C in 2 hours and held there for 2 hours. It was then cooled to about 100°C, aspirator vacuum was applied to the top of the condenser and the mixture reheated to 200°C. After 2 hours, it was allowed to cool.

After stripping by distillation to a flask temperature of 266°C under aspirator vacuum, the clear, water-white residue was vacuum-distilled. The product was a water-white, refractive oil, b.p. 178-201°C/0.03 mm, n_D^{24} 1.5718, d_4^{25} 1.2905. The molecular weight was 359 obsd; 360.5 calc. The yield was 312.9 gm, equivalent to 86.8%.

29. Phenyl m-trifluoromethylphenyl phosphate, (1:1). MLO 9593.

In a one-liter, 2-neck, round-bottom flask fitted with an 80 cm reflux condenser and thermowell was placed 141 gm (1.5 moles) of phenol, 243 gm (1.5 g) of m-trifluoromethylphenol, 169 gm (1.1 moles) of $POCl_3$ and 2.8 gm of powdered anhydrous $MgCl_2$. The mixture was heated to 200°C in the course of 2 1/4 hours and held there for 3 hours. Then the mixture was cooled to about 150°C, aspirator vacuum applied to the top of the condenser, and the mixture reheated to 200°C. After 2 1/2 hours it was allowed to cool.

The reaction product was stripped by distillation under aspirator vacuum to a flask temperature of 260°C. The head temperature reached 155°C and continued to rise. Taking into account the volatility of the product, the stripping was stopped at this point and the product vacuum-distilled.

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The product was a mobile, water-white refractive oil, b.p. 153-158°C/0.04 mm, n_D^{24} 1.5077, d_4^{25} 1.3567. The molecular weight was 424 obsd; 428 calc. The yield was 360.8 gm, or 84.4% of theory.

30. Phenyl m-trifluoromethylphenyl phosphate, (2:1). MLO 9594.

In a one-liter, 2-neck, round-bottom flask fitted with a thermowell and 80 cm reflux condenser was placed 94.8 gm (0.585 moles) of m-trifluoromethylphenol, 110 gm (1.17 moles) of phenol, 98.8 gm (0.644 moles) of POCl$_3$ and 0.75 gm (about 0.25 wt%) of anhydrous MgCl$_2$. The mixture was heated to 200°C in the course of 3 hours and maintained there for an additional 2 hours. It was allowed to cool to 150°C, aspirator vacuum applied to the top of the condenser, reheated to 200°C, held there for 1 1/2 hours and allowed to cool.

After stripping by distillation under aspirator vacuum to a flask temperature of 255°C, the residue was vacuum distilled. The product was a mobile, water-white, refractive oil, b.p. 153-157°C/0.03 mm, n_D^{23} 1.5248, d_4^{25} 1.3172. The molecular weight was 393 obsd; 394 calc. The yield was 194.6 gm or 84.2%.

31. Bis(triphenylsilyl) benzenephosphonate. MLO 9595.

In a one-liter, 2-neck, round-bottom flask equipped with a thermowell and reflux condenser was placed 414 gm (1.5 moles) of triphenylsilanol and 146.3 gm (0.75 moles) of benzenephosphonyl dichloride (Eastman P6547, redistilled). There was a negative heat of solution, then HCl started to evolve rapidly, and the mixture thinned out and started to foam, finally foaming out of the flask.

The run was then repeated, with the same weight of reactants, but using a 2-liter flask to give more expansion volume. The acid chloride was added to the silanol all at once and mixed with a stirring rod. A thick tan dough formed. Then the reaction started and HCl was copiously evolved. The dough thinned out to a viscous liquid which formed a foam with the HCl. The liquid was swirled and cooled in an ice bath to moderate the reaction. The mixture then resolidified but continued to liberate heat. After standing one hour, the mixture was slowly heated to 210°C. The molten liquid was brown and turbid. The solid on the walls of the flask reacted vigorously and evolved HCl when it became detached and fell into the hot liquid phase. After all the solid had disappeared, the mixture was kept at 210°C for 4 hours, cooled to 100°C, aspirator vacuum applied to the top of the condenser, reheated to 210°C and held there for 3 hours. It was allowed to cool, becoming a solid.

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Two vacuum-distillations gave 284.4 gm of product, a hard, light-yellow solid, b.p. 293-319°C/0.035 mm, m.p. 167-183°C. The yield of crude product was 56.6%. The solid had a strong acrylic ester odor.

On the first attempt at purification, a single crystallization from benzene gave a white solid, m.p. 184.5-189°C. On the second recrystallization a little ethanol was added to the boiling benzene solution. The recovered product melted sharply at 162-163°C. It appeared that alcoholysis had occurred.

A fresh sample, after two recrystallizations from benzene, was a white solid, m.p. 190-191°C (374-376°F). The solid was odorless. The molecular weight of this material was 687 obsd; 674 calc. This material, relatively insoluble in acetone, readily reacted with water to form an acetone-soluble substance.

Unsuccessful Preparations

32. Diphenylsilylene bis(diphenyl phosphate).

In a one-liter, 2-neck, round-bottom flask equipped with 80 cm spiral reflux condenser and thermowell was placed 322.2 gm (1.2 moles) of diphenyl phosphoryl chloride, 129.6 gm (0.6 mole) of diphenyl silanediol, and 2.7 gm of anhydrous $MgCl_2$. The reaction mixture was heated in 1.5 hours to 210°C. The evolution of HCl was brisk but controlled. On cooling, the reaction mixture was a light amber liquid. Aspirator vacuum was applied to the top of the condenser and the mixture heated to 210°C and held there for 7 hours to complete the reaction. After stripping to a flask temperature of 268°C under aspirator vacuum, the residue was vacuum-distilled.

No constant boiling product could be obtained. The material appeared to decompose upon distillation to a low-boiling material and a polymer. It seems likely that disproportionation occurred and such products as pyrophosphates, polysiloxanes and simple phosphates were formed.

33. Diphenyl triphenylsilyl phosphate.

Procedure A. To a solution of 276 gm (1.0 mole) of triphenyl silanol (used as received from Dow Corning Corporation) in one pound of pyridine was added portionwise 268.5 gm (1.0 mole) of diphenyl phosphoryl chloride. The temperature of the reaction mixture rose about 30°C. The mixture was then heated to about 109°, at which point the solution gave the appearance of boiling (steady

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bubble formation). On cooling the solution to room temperature, a precipi-
tate formed. The mixture was refrigerated, whereupon a thick slurry formed.

The slurry was vacuum-filtered. The filter cake was slurried seve-
ral times in anhydrous ether, and refiltered after each washing. The filtrate
and ether washings were combined and refrigerated.

The solid material was suspended in anhydrous ethanol, then filtered.
This treatment will dissolve pyridine hydrochloride. The filtrate was brown-
ish; the filter cake was white crystalline material. The crystals were washed
on the filter three times with absolute ethanol. The yield of crystalline pro-
duct was 201.6 gm. It was insoluble in cold benzene, partly soluble in hot
benzene, soluble in nitrobenzene on warming. It burned with a sooty flame.
The melting point was 227.5-229°C. It seems probable that the substance was
hexaphenyl disiloxane, m.p. 222°C.

The refrigerated filtrate was refiltered and a second crop of pyridine
hydrochloride and disiloxane obtained. Two more cycles of refrigeration and
filtration were carried out, with pyridine hydrochloride and disiloxane being
obtained each time as a precipitate.

The final filtrate, on attempted distillation, after removal of volatiles,
appeared to decompose and a solid residue was left in the flask. The distil-
late consisted of solid material and white fumes distilling to a head tempera-
ture of 213°C/0.175 mm. This distillate could not be redistilled.

Procedure B. (1). Diphenyl hydrogen phosphate. A mixture of 652 gm
(2.0 moles) of triphenyl phosphate and 160 gm (4.0 moles) of NaOH dissolved
in 1600 ml of water was refluxed for 8-9 hours at 105°C whereupon a single-
phase solution resulted. The solution was filtered and acidified in two por-
tions with 800 ml of 6N HCl. An oil phase separated out and solidified when
cooled and seeded. The pinkish solid was vacuum-filtered and washed three
times with ice-water. A pinkish oil washed out leaving colorless crystalline
solid. The oil weighed 164 gm. The white product, diphenyl hydrogen phos-
phate dihydrate, was dried at room temperature; the melting point was 50-
52°C. The yield was 387 gm, equivalent to 67.6%.

The diphenyl hydrogen phosphate dihydrate was dehydrated by reflux-
ing in 500 cc of dry benzene. Two phases formed; the water phase was sepa-
rated off and the benzene phase dried over anhydrous $MgSO_4$. The benzene
was evaporated off, finally under reduced pressure. The oil crystallized,

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when refrigerated, to a solid, m.p. 63.5°C. The solid was dissolved in warm benzene and petroleum ether added to the point of incipient turbidity. On cooling, a two-phase system formed. When refrigerated, a white solid precipitated out. The solid product was then filtered off and dried.

(2). In two portions, a solution of 183.3 gm (0.733 moles) of diphenyl hydrogen phosphate in one pound of pyridine was added to a suspension of 215.9 gm (0.733 moles) of triphenyl chlorosilane in one pound of pyridine. There was no heat liberated. The mixture was heated to reflux and allowed to cool, then refrigerated for 1-2 days.

The precipitate which formed was filtered off and washed with absolute ether. The precipitate proved to be insoluble in water and ethanol. After being washed three times with ethanol and once with ether, the solid was air dried. The m.p. was 228-229.5°C. The mixed m.p. with the solid obtained from the first-attempted diphenyl triphenylsilyl phosphate preparation was 228-229°C. Thus the material was the same as the first, probably hexaphenyl disiloxane.

The ether washings and original filtrate gave heavy crops of crystals on standing. The solid was readily soluble in water. When an aqueous solution of the crystals was acidified with dilute HCl, an oil formed, which crystallized into a solid, m.p. 48-53°C, when refrigerated. This appeared to be diphenyl hydrogen phosphate dihydrate.

Procedure C. In a one-liter, 2-neck, round-bottom flask equipped with a thermowell and 80 cm spiral water-cooled reflux condenser was placed 194.2 gm (0.704 moles) of triphenylsilanol and 189.0 gm (0.704 moles) of diphenyl phosphoryl chloride. No catalyst was used. The acid chloride rapidly wetted-out the silanol powder. The mixture was heated to 200°C in the course of 2 hours and held there for an additional 2 hours. During the heating, HCl was evolved. The mixture was black or dark brown. The mixture was cooled to 130°C and aspirator vacuum applied to the top of the condenser. Heating was resumed, the temperature reaching 200°C in one hour. This temperature was held for nine hours, then the mixture was allowed to cool.

After stripping the reaction mixture to a flask temperature of 290°C under aspirator vacuum, the residue was subjected to a series of vacuum-distillations, filtrations and recombinations to yield the following series of fractions (pressure corrected to 0.04 mm).

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Fract.	B.p., °C/0.04 mm	Flask T, °C	Weight	Appearance
1 b	152-156	to 179	6.8	Lt. yel. pungent liquid
2 b	156-158	to 182	8.7	Lt. yel. pungent liquid
3 b	158-160	to 188	21.5	Lt. yel. pungent liquid
4 b	160-167	to 214	12.3	Lt. yel. pungent liquid
1 c	165-169	243-260	30.1	White solid
2 c	169	260-288	14.5	White solid
3 c	169-230	288-306	7.0	Solid & liquid
4 c	230-242	302-310	9.0	Solid & liquid
5 c	242-243	-345	63.9	Viscous liquid

When cumulative weight distilled was plotted against boiling point, three plateaus were observed. These were 3 b, 2 c, and 5 c. Fraction 3 b was a pungent oil, n_D^{25} 1.5802, molecular weight 334 obsd; and gave a positive Beilstein halogen test.

Fraction 2 c was a solid which gave a negative Beilstein halogen test and had an observed molecular weight of 333.

Fraction 5 c was the most intensively examined. On an attempted molecular weight determination, a small proportion of benzene-insoluble residue remained undissolved. The fraction was filtered. The filtrate had a molecular weight of 490, n_D^{25} 1.5866 (very diffuse) and gave a negative Beilstein test. On standing for a week or two, most of the fraction crystallized. It was refiltered, the precipitate being retained. This had a molecular weight of 545. It was not further characterized.

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C. Oxidation Tests

1. These tests were purely qualitative. In the first test a 150 cc beaker containing 50 gm of tris(o-chlorophenyl) phosphate + 0.5 gm diphenyl 3-pyridyl phosphate was heated at an average temperature of about 550°F on a hotplate. The control was a 50 gm sample of tris(o-chlorophenyl) phosphate with no additive. The test was interrupted after 95 minutes, at which time the test sample was light yellow and clear, with no sludge deposition. The control was cloudy but colorless and had also deposited no sludge. The test was resumed after an interval of 15 1/2 hours, and upon reaching 550°F, the test sample deposited considerable sludge, and had become cloudy and colorless. The control was cloudy and colorless. It is thought that moisture pickup occurred during the interval. The weight loss of the test sample after 345 minutes was 72.7%, while the weight loss of the control was 86.3%. The conclusion is drawn that the additive was effective as an inhibitor until the test was interrupted, and even so, there was less weight loss of the test sample over-all.

2. The second test was run in two parts. In the first part, the samples were 7 cc of tris(o-chlorophenyl) phosphate and 7 cc of tris(m-chlorophenyl) phosphate in 20 cc beakers. Test temperature was approximately 500°F. During the test, the ortho compound stayed light-colored but became cloudy. Sludge deposition was moderate. The meta compound turned dark in less than 1/2 hour and deposited more sludge. After about 4 hours, both had evaporated to dryness. Sludge was deposited on sides and bottoms of both beakers in about the same amount.

In the second part, the test sample was 7 cc of tris(m-chlorophenyl) phosphate + 0.2 cc of diphenyl 3-pyridyl phosphate in a 20 cc beaker. The temperature was about 500°F. After 2 hours the sample was light yellow, slightly hazy, and had deposited a thin layer of sludge on the bottom of the beaker but none on the sides. The color then darkened slowly and sludge deposition increased with time until at 6 hours the beaker was dry, with a black varnish deposit. The conclusion is drawn that the additive showed definite antioxidant properties, since darkening and volatilization of the sample was very much slower and sludge deposition much less.

V. NOTEBOOK REFERENCES

The data from which this report was compiled are contained in Southwest Research Institute Notebooks Nos. 126, 608, 609, 610, 632 and 655.

VI. BIBLIOGRAPHY

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APPENDIX

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TABLE I. PHYSICAL PROPERTIES OF COMPOUNDS PREPARED

Compound	MLO Number	Bp, °C/mm (obsd)	Calc NBP °C(°F)	d_4^{25}	n_D^t	Therm Decomp Temp °C(°F)	Viscosity, cs 100°F	210°F	400°F	700°F	ASTM Slope 100°-210°F	210°-400°F	400°-700°F	Mp, °C (°F)	Pour Pt, °F	Mol Wt obsd(calc)	Vapor Pressure, mm 210°F	400°F	700°F
Bis(o-chlorophenyl) p-chlorophenyl phosphate	9565	202-203/0.035	457(854)	1.4063	1.5806$^{27.0}$	>467(873)	49.6	4.86	1.09	0.406	0.916	0.910	0.978	43-45(109-113)	- - -	422(429.5)	7x10^{-4}	0.44	143
Bis(p-chlorophenyl) o-chlorophenyl phosphate	9566	205/0.05	457(854)	1.4083	1.5803$^{27.0}$	>468(874)	44.7	4.59	1.05	0.337	0.925	0.916	1.22	48-50(118-122)	- - -	424(429.5)	6x10^{-5}	0.18	138
Tetrakis(m-tolyl) pyrophosphate	9567	252-265/0.03	494(921)	1.2331	1.5517$^{27.0}$	333(631)	85.9	8.34	1.74	- -	0.778	0.748	- -	- -	-10	547(538)	5x10^{-4}	0.02	- -
Tris(chlorophenyl) phosphate, (1:1 ortho-para)	9568	215-217/0.03	457(854)	1.4083	1.5806$^{26.5}$	>468(874)	47.7	4.76	1.08	0.343	0.919	0.919	1.22	(2-phase)	(2-phase)	422(429.5)	9x10^{-5}	0.28	140
Tris(chlorophenyl) phosphate, (2:1 ortho-para)	9569	191-208/0.03	456(853)	1.4081	1.5811$^{26.5}$	>468(874)	52.0	4.99	1.11	0.405	0.914	0.905	0.992	- -	0	430(429.5)	3.5x10^{-4}	0.35	140
Tris(chlorophenyl) phosphate, (4:1 ortho-para)	9570	209-214/0.03	458(856)	1.4084	1.5814$^{26.5}$	>468(874)	56.0	5.27	1.16	0.416	0.902	0.895	0.984	- -	0	423(429.5)	3.5x10^{-4}	0.35	137
Tris(chlorophenyl) phosphate, (5:1 ortho-para)	9571	201-208/0.03	458(856)	1.4076	1.5816$^{26.5}$	>468(874)	56.7	5.38	1.17	0.353	0.895	0.892	1.23	- -	0	429(429.5)	3.5x10^{-4}	0.35	132
Tetraphenyl pyrophosphate	9572	223-235/0.02	477(890)	1.2963	1.5592$^{26.5}$	362(684)	45.2	6.39	1.48	- -	0.744	0.770	- -	- -	-15	485(482)	4.7x10^{-4}	0.02	- -
Bis(o-chlorophenyl) m-trifluoromethylphenyl phosphate	9573	157/0.04	378(712)	1.4264	1.5185$^{25.0}$	>383(721)	22.3	3.37	0.87	- -	0.901	0.953	- -	- -	-30	461(463)	8.7x10^{-4}	3.3	630
Diphenyl o-chlorophenyl phosphate	9574	167-168/0.05	424(795)	1.2892	1.5716$^{23.5}$	441(826)	19.5	3.52	0.97	0.321	0.828	0.873	1.23	- -	-30	357(360.5)	5.7x10^{-4}	1.7	275
Bis(o-chlorophenyl) m-trifluoromethylphenyl phosphate	9575	171-179/0.025	377(710)	1.4171	- - -	>394(741)	25.9	3.60	0.91	0.294	0.905	0.941	1.33	51-53(124-127)	- - -	460(463)	8.5x10^{-4}	4.0	670
Bis(o-chlorophenyl) phenyl phosphate	9576	178-179/0.035	435(815)	1.3468	1.5767$^{26.0}$	>454(849)	32.2	4.40	1.10	0.344	0.851	0.863	1.21	- -	-20	391(395)	1.0x10^{-3}	0.70	220
o-chlorophenyl m-trifluoromethylphenyl phosphate, (4:1)	9577	172-203/0.05	418(784)	1.4156	1.5540$^{26.0}$	>429(904)	40.6	4.53	1.04	0.381	0.901	1.05	0.920	- -	5	455(450)	1.0x10^{-3}	1.0	310
Phenyl o-chlorophenyl phosphate, (1:1)	9578	171-186/0.05	427(800)	1.3132	1.5731$^{26.0}$	>441(826)	23.9	3.87	0.80	0.329	0.828	1.10	1.05	- -	-25	36(378)	1.6x10^{-3}	1.2	260
Phenyl o-chlorophenyl phosphate, (1:2)	9579	180-195/0.05	440(824)	1.3431	1.5747$^{30.0}$	>454(849)	30.9	4.35	1.07	0.400	0.845	0.873	0.879	- -	-25	392(395)	8.0x10^{-4}	0.65	200
Bis(o-chlorophenyl) m-chlorophenyl phosphate	9580	188-194/0.03	455(851)	1.3993	1.5795$^{25.5}$	>468(874)	36.1	4.36	1.04	0.392	0.890	1.04	0.993	48-50(118-122)	- - -	429(429.5)	5.4x10^{-4}	0.43	140
Bis(o-chlorophenyl) m-chlorophenyl phosphate	9581	195/0.02	448(838)	1.4029	1.5819$^{24.0}$	>468(874)	42.7	4.79	1.11	0.352	0.881	0.889	1.20	- -	5	431(429.5)	3.5x10^{-3}	1.1	173
Tris(chlorophenyl) phosphate, (1:1 ortho-meta)	9582	192-201/0.06	453(847)	1.4005	1.5797$^{24.5}$	>468(874)	36.7	4.46	1.06	0.405	0.882	0.902	0.961	- -	-20	430(429.5)	6.4x10^{-4}	0.45	149
Tris(chlorophenyl) phosphate, (1:2 ortho-meta)	9583	193-196/0.06	454(849)	1.4050	1.5755$^{26.0}$	>468(874)	45.1	4.97	1.12	0.354	0.884	0.896	1.19	- -	-15	430(429.5)	2.2x10^{-3}	0.80	155
Bis(m-chlorophenyl) p-chlorophenyl phosphate	9584	197/0.04	447(837)	1.3833	1.5790$^{23.0}$	>468(874)	31.6	4.12	1.00	0.335	0.880	0.918	1.19	- -	-20	433(429.5)	6x10^{-4}	0.45	165
Bis(m-chlorophenyl) phenyl phosphate	9585	175-176/0.08	458(856)	1.3413	1.5741$^{23.0}$	>441(826)	19.5	3.47	0.96	0.322	0.832	0.876	1.22	- -	-25	396(395)	-9x10^{-4}	0.75	253
Bis(m-chlorophenyl) phenyl phosphate	9586	195/0.10	445(833)	1.4065	1.5790$^{26.0}$	>454(849)	33.2	4.27	1.04	0.348	0.889	0.899	1.16	- -	-20	434(429.5)	1.7x10^{-4}	0.60	159
Tris(chlorophenyl) phosphate, o-chlorophenyl phosphate, (1:2 ortho-meta)	9587	193/0.05	442(828)	1.4067	1.5797$^{24.0}$	>454(849)	33.6	4.29	1.03	0.402	0.877	0.905	0.951	- -	-10	433(429.5)	3.5x10^{-3}	0.26	190
Phenyl o-chlorophenyl m-chloro-phenyl phosphate, (1:1:2)	9588	183-207/0.05	429(804)	1.3622	1.5755$^{26.0}$	>441(826)	24.1	3.75	0.98	0.331	0.857	0.900	1.19	- -	-25	401(404)	2.6x10^{-4}	0.55	255
Phenyl o-chlorophenyl m-chloro-phenyl phosphate, (1:1:3)	9589	186-199/0.04	437(819)	1.3833	1.5790$^{23.0}$	>454(849)	32.8	4.30	1.04	0.403	0.868	0.902	0.955	- -	-15	413(412)	2.5x10^{-2}	3.1	250
Phenyl o-chlorophenyl 4-biphenylyl phosphate, (1:3:1)	9590	192-274/0.04	458(856)	1.3493	1.5938$^{25.0}$	>468(874)	85.1	6.80	1.29	0.409	0.875	0.902	1.08	- -	+10	426(434)	2.6x10^{-3}	0.75	130
Tris(chlorophenyl) phosphate, (1:1:1 ortho-meta-para)	9591	204-206/0.03	443(829)	1.4057	1.5822$^{20.0}$	>454(849)	37.5	4.39	1.06	0.401	0.897	0.892	0.976	- -	-10	434(429.5)	6.5x10^{-4}	0.56	196
Phenyl o-chlorophenyl phosphate, (2:1)	9592	178-201/0.03	417(782)	1.2905	1.5718$^{24.0}$	>429(804)	19.5	3.52	1.02	0.397	0.828	0.825	0.962	- -	-30	359(360.5)	1x10^{-2}	2.3	335
Phenyl m-trifluoromethyl-phenyl phosphate, (1:1)	9593	153-158/0.04	369(696)	1.3567	1.5077$^{24.0}$	>383(721)	11.3^b	2.40	0.75	0.403	0.892	0.927	0.688	- -	-50	424(428)	3x10^{-2}	7.0	820
Phenyl m-trifluoromethyl-phenyl phosphate, (2:1)	9594	153-157/0.03	375(707)	1.3172	1.5248$^{23.0}$	>383(721)	11.5^c	2.50	0.80	0.330	0.866	0.879	1.04	- -	-45	393(394)	9x10^{-3}	4.5	720
Bis(triphenylsilyl) benzenephosphonate	9595	293-319/0.035	482(900)	- - -	- - -	441(826)	- -	- -	- -	- -	- -	- -	- -	190-191(374-376)	- - -	687(674)	2x10^{-6}	0.014	31

^{a} Normal boiling point.
^{b} Viscosity @ -40°F, 328,000 cs, Slope -40-100°F, 1.12.
^{c} Viscosity @ -40°F, 260,000 cs, Slope -40-100°F, 1.11.

TABLE II. SECONDARY PROPERTIES OF PROMISING COMPOUNDS

Compound	MLO Number	Flash Pt, °F	Fire Pt, °F	Auto Ign Temp °F	Solubilities, gm/100 gm @ °C[a] Aliph Naphtha	DC 550	Hydrolytic Stability Data Wt % Insolubles	Cu Loss mg/cm²	Vis Oil @ 100°F	Vis Oil @ 210°F
Tris(chlorophenyl) phosphate, (2:1 ortho-para)	9569	550	>760	>1400	26.4 @ 24	370 @ 25	0.061	12.8	20.1	3.32
Tris(chlorophenyl) phosphate, (4:1 ortho-para)	9570	545	>760	>1400	21.7 @ 26	241 @ 26	--[b]	--[b]	--[b]	--[b]
Tris(chlorophenyl) phosphate (5:1 ortho-para)	9571	550	>760	>1400	18.0 @ 27	198 @ 25	--[b]	--[b]	--[b]	--[b]
Diphenyl o-chlorophenyl phosphate	9574	505	>760	1319-1418	16.2 @ 29	147 @ 26	0.034	12.8	30.6	4.32
Bis(o-chlorophenyl) phenyl phosphate	9576	520	>760	>1400	15.0 @ 26	134 @ 26	0.053	11.5	20.2	3.20
Phenyl o-chlorophenyl phosphate, (1:1)	9578	500	>760	>1400	15.2 @ 27	146 @ 26	0.080	12.2	19.5	3.10
Phenyl o-chlorophenyl phosphate, (1:2)	9579	530	>760	>1400	16.6 @ 29	133 @ 26	0.080	16.4	18.1	2.94
Bis(o-chlorophenyl) m-chlorophenyl phosphate	9581	550	>760	>1400	54.0 @ 30	400 @ 26	0.116	15.3	14.4	2.39
Tris(chlorophenyl) phosphate, (1:1 ortho-meta)	9582	560	>760	>1400	129 @ 25	inf	0.032	9.3	15.3	2.55
Tris(chlorophenyl) phosphate, (2:1 ortho-meta)	9583	560	>760	>1400	42.0 @ 28	395 @ 27	0.112	13.8	10.4	1.87
Bis(m-chlorophenyl) p-chlorophenyl phosphate	9584	550	>760	>1400	inf	inf	0.020	12.0	25.0	3.65
Bis(m-chlorophenyl) phenyl phosphate	9585	520	>760	>1400	inf	inf	0.006	11.2	21.7	3.50
Bis(m-chlorophenyl) o-chlorophenyl phosphate	9586	510	>760	>1400	inf	inf	0.050	14.7	16.8	2.72
Tris(chlorophenyl) phosphate, (1:2 ortho-meta)	9587	545	>760	>1400	inf	inf	0.070	15.7	13.6	2.40
Phenyl o-chlorophenyl m-chlorophenyl phosphate, (1:1:2)	9588	510	>760	>1400	95.7 @ 25	inf	0.080	16.6	14.3	2.56
Phenyl o-chlorophenyl m-chlorophenyl phosphate, (1:3:2)	9589	525	>760	>1400	32.6 @ 28	inf	0.010	7.3	10.5	2.01
Phenyl o-chlorophenyl 4-biphenylyl phosphate, (1:3:1)	9590	540	>760	>1400	11.6 @ 27	34.3 @ 25	0.020	4.8	18.1	2.84
Tris(chlorophenyl) phosphate, (1:1:1 ortho-meta-para)	9591	540	>760	>1400	inf	inf	0.060	14.6	16.0	2.67
Phenyl o-chlorophenyl phosphate, (2:1)	9592	510	>760	>1400	12.2 @ 25	>100 @ 25	0.050	14.8	20.6	3.33
Phenyl m-trifluoromethylphenyl phosphate, (1:1)	9593	450	715	>1400	inf	inf	0.004	11.4	7.6	1.66
Phenyl m-trifluoromethylphenyl phosphate, (2:1)	9594	485	735	>1400	inf	inf	0.002	11.5	11.2	2.25
Special Tests										
Tris(o-chlorophenyl) phosphate	9522	560	>760	>1400	15.5 @ 28	- - -	0.003[c]	- -	10.0	2.02
Tris(o-chlorophenyl) phosphate	9522						0.036[d]	13.0	11.0	2.18
Tris(m-chlorophenyl) phosphate	9553	540	>760	>1400	inf	- - -	0.003[c]	- -	25.2	4.02
Tris(m-chlorophenyl) phosphate	9553						0.006[d]	11.1	21.5	3.55

[a] All compounds insoluble in hot and cold water; infinitely soluble in C_6H_6, trichloroethylene and di-2-ethylhexyl sebacate.
[b] Not tested. Refer to MLO 9569.
[c] Without Cu strip.
[d] With Cu strip.